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ERRATTA.

Page	
17-19	Tables VI to VII for "supernateut" read "supernatant."
32	line 1* for "eampene" read "camphene."
39	,, 11* for "Point-o-lite" read "Point-o-lite."
63	,, 10 for "Taluamidine" read "Toluamidine."
66	,, 14* for "consideration" read "condensation."
73	,, 11* omit "yellow."
73	,, 10* insert "yellow" between "The" and "prismatic."
116	,, 9 Insert "ammonia and the alkali metals and chlorides and nitrates of" between "of" and "calcium."
240	,, 5 for "Peacock" read "Peacock."
250	,, 12* for 3×10^{-x} read 3×10^{-z}
265	,, 10* for 6°C read 26°C

* From bottom

The Reduction of the Group -CH(OH)-CCl₃.

Part I

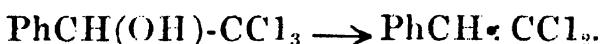
BY

ANDREW NORMAN MELDRUM

AND

RUPCHAND LILARAM ALIMCHANDANI

The reduction of trichloromethyl carbinols was studied by Jocitsch (J. Russ. Chem. Soc., 1898, 30, 920-924) and Jocitsch and Favorsky, (*ibid*, 990-1003)¹ with the result that the products were found to be derivatives of dichloroethylene: for instance, phenyl trichloromethyl carbinol gave dichloro-styrene:



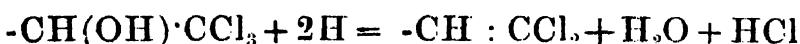
The reduction was carried out in boiling alcoholic solution and the best results were obtained by taking, not the carbinol itself, but its acetyl derivative, and using zinc in the form of shavings. (Jocitsch and Favorsky, *loc. cit.*).

Jocitsch's method of reduction leads to the conversion of the group -CH(OH).CCl₃ into -CH : CCl₂ and of >C(OH).CCl₃ into >C : CCl₂. Following on this change chlorine atoms were sometimes replaced by hydrogen. Thus acetone-chloroform on reduction gave three products, namely, dichloro*iso*-butylene, *isocrotylic chloride*, and *isobutylene*:

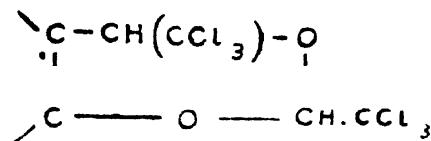


¹ The original papers are not easily accessible and are known to us only in abstract. For the papers cited above see *Jour. Chem. Soc.*, 1899, 76, I, 748; 786; or numerous papers on the synthesis and reduction of trichloromethyl carbinols that were published by Jocitsch from 1902 to 1906, see *loc. cit.*, 1914, 106, i, (under the spelling Jocitsch).

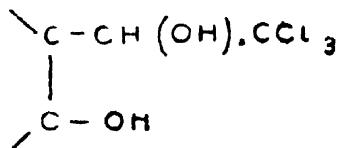
For the present purpose it is not necessary to consider tertiary alcohols that contain the group $>\text{C}(\text{OH})\cdot\text{CCl}_3$. The scope of this paper is limited to secondary alcohols containing the group $-\text{CH}(\text{OH})\cdot\text{CCl}_3$; this group can be reduced to $-\text{CH}_2\cdot\text{CHCl}_2$ as Jocitsch's work has proved:—



The authors observed indications that the group $-\text{CH}(\text{OH})\text{CCl}_3$, under different conditions from those employed by Jocitsch, can be reduced to $-\text{CH}_2\cdot\text{CHCl}_2$, the reducing agent that was employed was zinc dust and acetic acid. A condensation product of *p*-cresotic acid and chloral, having the formula $\text{C}_{12}\text{H}_8\text{O}_4\text{Cl}_6$, was converted by reduction into the substance $\text{C}_{10}\text{H}_{10}\text{O}_3\text{Cl}_2$. This was explained as follows:—the substance of formula $\text{C}_{12}\text{H}_8\text{O}_4\text{Cl}_6$ contains the heterocyclic ring



which is hydrolysed to



and chloral and then the reduction proceeds thus:—
 $-\text{CH}(\text{OH})\text{CCl}_3 + 4\text{H} = -\text{CH}_2\cdot\text{CHCl}_2 + \text{H}_2\text{O} + \text{HCl}$. (T., 1921, 119, 204). The reduction product was easily obtained and it appeared that the group $-\text{CHCl}_2$ is almost inert towards the reducing agent.

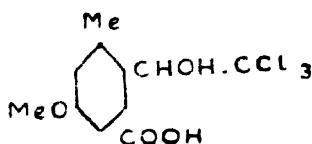
Whilst this explanation is sufficient and satisfactory as far as it goes, it is true that it turns into an intermediate product, which was not isolated, and that better evidence might be forthcoming on the subject. The

authors have made a beginning with the study of the numerous compounds that contain the group -CH(OH)·CCl₃ and have found various cases in which this group is changed into -CH₂·CHCl₂. The cases reported in this paper can be classified as follows:—

- I. DERIVATIVES OF *m*-CRESOTIC ACID;
- II. $\gamma\gamma\gamma$ -TRICHLORO-- β --HYDROXY-BUTYRIC ACID;
- III. DERIVATIVES OF UREA, THIOUREA, URETHANE AND URETHYLANE.

I. DERIVATIVES OF *m*-CRESOTIC ACID.

*3-methoxy - 6 - α - hydroxy-βββ-trichloroethyl-p-toluic acid.*¹



The solution obtained by shaking together 3-methoxy-*p*-toluic acid (58 grams), chloral hydrate (74 grams) and sulphuric acid (97 per cent., 275 c. c.) was kept for three days and then poured over ice. A white deposit was formed which was crystallised from glacial acetic acid and then for analysis, from acetone: prisms mp. 236-237°, with effervescence. (Found: Cl=33.78; equivalent =312.7; C₁₁H₁₁O₄Cl₃ requires Cl=33.95; equivalent=313.5).

The *calcium salt* (prismatic needles) crystallises with 10 molecules of water of crystallisation. Two different samples were analysed. (Found: Ca=4.74: 4.74; (C₁₁H₁₁O₄Cl₃)₂Ca·10H₂O requires Ca=4.74 per cent.).

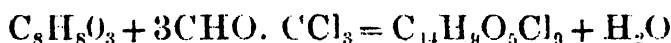
The *acetyl derivative* (crystalline powder) melts at 203-204°. (Found: equivalent =355.5; C₁₃H₁₃O₅Cl₃ requires equivalent =355.5).

¹ The authors, by work that will be described in a later paper, have proved this substance to have the constitution ascribed to it above.

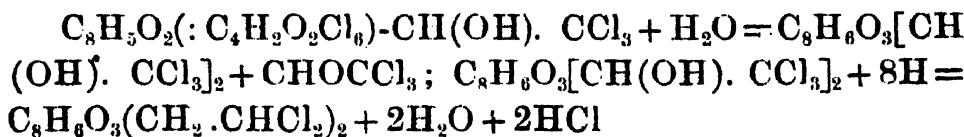
3-methoxy-6 ββ-dichloroethyl-p-toluic acid.

To the hot solution of the trichloromethyl carbinol (2 grams) in acetic acid (10 c. c.), zinc dust (2·5 grams) was added little by little: the heating was continued for about 15 minutes. The liquid was filtered and water was added to the filtrate: white leaflets were obtained which after crystallisation from methyl alcohol melted at 166-167°. (Found: Cl = 26·86; equivalent = 262; C₁₁H₁₂O₃Cl₂ requires Cl = 26·96; equivalent = 263).

The authors have studied also a substance that is produced in the condensation of chloral with *m*-cresotic acid. As the main product of this condensation Schleusner and Voswinckel (*Annalen.*, 1921, 422, 111) obtained amorphous material, from which, by a series of changes, that ended with methylation of the phenolic group, they obtained the methyl ether of γ-coccinic acid (Meldrum. T., 1911, 99, 1712). The amorphous material, the authors find, contains at least one crystalline substance formed according to the equation:



On reduction it yields a crystalline substance C₁₂H₁₂O₃Cl₄. This change can be explained thus: the substance C₁₄H₉O₅Cl₉ is C₈H₅O₂(:C₄H₂O₂Cl₆)-CH(OH). CCl₃, that is, it contains the cresotic acid residue and (1) the heterocyclic ring that is present in the *p*-cresotic acid derivative already mentioned; (2) the group-CH(OH). CCl₃, that is present in the chloral derivative of the methyl ether of *m*-cresotic acid. When the heterocyclic ring is hydrolysed the product contains two-CH(OH). CCl₃ groups that can be reduced.



Condensation of m-cresotic acid and chloral.

The solution obtained by shaking together *m*-cresotic acid (16 grams), chloral hydrate (50 grams) and sulphuric acid (97 per cent., 100 c.c.) was kept for three days and then poured on ice. A gelatinous mass separated which was washed and dried. When it was dissolved in dilute acetic acid, a small amount of a crystalline powder separated. This was re-crystallised from methyl alcohol; glistening plates mp. 211-212°. (Found : Cl=55.20 ; C₁₄H₉O₅Cl₉ requires Cl=55.38 per cent.).

Reduction of the substance C₁₄H₉O₅Cl₉

To the hot solution of the substance C₁₄H₉O₅Cl₉ (2 grams) in glacial acetic acid (20 c.c.) zinc dust (5 grams) was added in small amount. The mixture was boiled for 15 minutes, and then filtered. When the filtrate was diluted with water, a substance separated in white leaflets. It was recrystallised from benzene for analysis : mp. 164-165° (Found Cl=41.3 ; C₁₂H₁₂O₅Cl₄ requires Cl=41.0 per cent.).

The calcium salt crystallises in needles. (Found : Ca=5.54 ; (C₁₂H₁₁O₃Cl₄)₂Ca requires Ca=5.49 per cent.).

II. CCl₃.CHOH.CH₂.COCH γγγ-Trichloro-β-hydroxy-butyric acid CHCl₂.CH₂.CH₂.COOH γγ-Dichloro butyric acid.

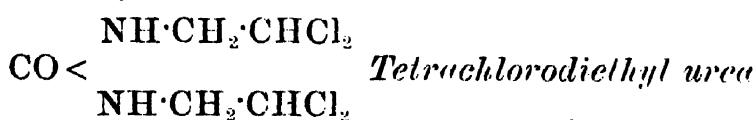
After preliminary experiments had been made on the reduction of γγγ-trichloro-β-hydroxy-butyric acid and of its ethyl ester the reduction was carried out using the methyl ester. (mp. 65-66°; Auwers and Schmidt (Ber., 1913, 46, 487) give 61-62°).

The methyl ester (30 grams) was dissolved in glacial acetic acid (100 c.c.); the solution was stirred mechanically whilst zinc dust (15 grams) was gradually added at such a rate that the temperature of the mixture did not

rise above 60°. The process lasted about an hour. Zinc acetate and unchanged zinc were removed by filtration and the filtrate when diluted with water, yielded a heavy oil (16 grams). This oil was dissolved in ether, washed with water, dried and distilled under reduced pressure: bp. 95-100°/36 mm. It is an unstable substance and was not obtained pure even by repeated distillation. (Found: Cl=39.2; C₅H₈O₂Cl₂ requires Cl=41.5; C₅H₇O₃Cl₃ requires Cl=48.1 per cent.). It was hydrolysed by shaking a mixture of the oil (5 grams) with a 10 per cent. sodium hydroxide solution (50 c.c.) for about 10 minutes, when the oil disappeared. On acidification of the solution a solid was obtained (0.5 gram) which was purified by crystallisation from water: shining leaflets mp. 103-104°. (Found: Cl=45.20; C₄H₆O₂Cl₂ requires Cl=45.21 per cent.).

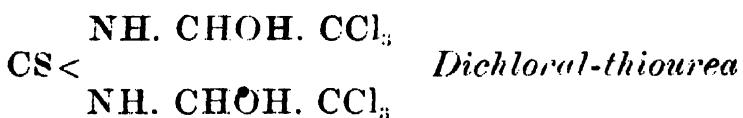
This acid and its esters will be investigated further. The acid itself is stable whilst the esters and the salts are unstable. The methyl and ethyl esters at ordinary temperature give off pungent vapours; and on distillation there is always a residue that crystallises. When the acid is treated with sodium hydroxide solution, there are unmistakable signs that the -CHCl₂ group is hydrolysed: this accounts for the small yield of the acid that was obtained when the methyl ester was hydrolysed.

III. Derivatives of urea, thiourea, urethane and urethylene



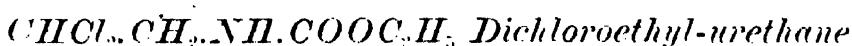
Dichloralurea has been obtained by Jacobsen (*Annalen.*, 1871, 157, 247). This substance (3 grams) being sparingly soluble in glacial acetic acid was suspended in that liquid (35 c.c.). Zinc dust (4 grams) was added with the same precautions as were observed in the case just mentioned. The reaction was slow; even after continuing the

process for about four hours, zinc (2·5 grams) remained unattacked. The filtered liquid after dilution gave needle shaped crystals (0·5 gram). The substance was recrystallised from alcohol for analysis: mp. 222° with decomposition. (Found : Cl = 55.86 ; C₅H₁₀ON₂Cl₄ requires Cl = 55.85 per cent.).



This was prepared by heating a mixture of thiourea (7 grams) and chloral (32 grams) : vigorous reaction took place. After washing the product with hot water, it was crystallised from a mixture of ether and benzene : crystalline powder mp. 150-151° with decomposition. (Found : Cl = 57·31 ; C₅H₆O₂N₂SCl₆ requires Cl = 57·35 per cent.)

The reduction product, namely, *detrachlorodiethyl-thiourea* was obtained in exactly the same manner as the corresponding urea derivative. From benzene it crystallises in lustrous leaflets mp. 162-163° with decomposition. (Found : Cl = 52·72 ; S = 11.73 ; C₅H₈SN₂Cl₄ requires Cl = 52.50 ; S = 11.87 per cent.).



Chloral urethane was prepared by Bischoff's method (*Ber.* 1874, 7, 6314). It melts at 106-108° (Bischoff gives 103°). To the solution of this substance (38 grams) in glacial acetic acid (150 c. c.) zinc dust (24 grams) was added with the same precautions as before. The reaction mixture was filtered and ice was added to the filtrate. An oil separated at first which crystallised when it was cooled by a freezing mixture. The solid was separated using a funnel cooled by ice and was dissolved in ether, washed with very dilute sodium carbonate solution, dried and distilled under reduced pressure : bp. 125-128°/23 m.m.

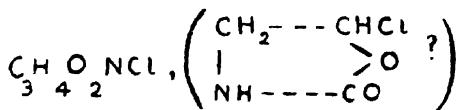
The solid melts at about 13° . (Found : Cl=37.54; $C_5H_6O_2NCl_2$ requires Cl=38.13 per cent.).

CCl₃CH(OH).NHCOOCH₃ *Chloral urethane*

Urethane (156 grams) and chloral (96 grams) dissolved rapidly in conc. hydrochloric acid (96 c. c.). The solid product separated in about half an hour. To the filtrate, chloral (48 grams) was added when another crop of the same substance was obtained. A fresh charge of chloral (24 grams) was again added. The collected yield of the condensation product was 267 grams. From chloroform it crystallises in rhombic plates : mp. $125-128^{\circ}$. (Found : Cl=47.80; $C_4H_6O_3NCl_3$ requires Cl=47.84 per cent.).

CHCl₂.CH₂.NH.COOCCH₃ *Dichloroethyl-urethane*

Chloral urethane (132 grams) was dissolved in acetic acid (530 c. c.). Zinc dust (76 grams) was added with the same precautions as before. The filtrate after dilution with water gave needle shaped crystals which when recrystallised from alcohol melted at $90-93^{\circ}$. (Found : Cl=41.10; $C_4H_7O_2NCl_2$ requires Cl=41.23 per cent.).



The solution obtained by dissolving dichloroethyl urethane (2 grams) in dry ether (20 c. c.) was saturated with dry HCl. After keeping for two days, it was slowly evaporated on the water bath when a syrupy liquid was obtained. When dissolved in hot benzene it crystallises in clusters of tiny needles : mp. $118-120^{\circ}$. (Found : Cl=29.38; $C_3H_4O_2NCl$ requires Cl=29.18 per cent.).

Part of the expense of this investigation was defrayed by a grant from the Syndicate of the University of Bombay.

Work on the substances that are described in this paper and on other trichloromethyl carbinols is being continued.

DEPARTMENT OF ORGANIC CHEMISTRY,
THE ROYAL INSTITUTE OF SCIENCE,
BOMBAY.

[Received 3rd February, 1925].

The Protective Action of Soaps and Further Evidence in favour of the Chemical Theory of Adsorption.

Part III

BY

S. S. BHATNAGAR, MATA PRASAD AND D. C. BAHL.

Zsigmondy (The Chemistry of Colloids, p. 112, 1917), has found that when gelatine is adsorbed by a thin foil of gold, it loses the property of solution in hot water. He, therefore, concludes that the protective action of soaps cannot be satisfactorily explained by simple thermodynamical reasoning. He believes that some chemical forces play an important part in the process of adsorption.

Bhatnagar and Srivastava (Journ. Phys. Chem., 28, 730, 1924) have studied the protection of sols and fine precipitates by sugars. They found that the optical rotation of a mixture of sugar solution and sol was not the same as expected on Beer's Law but was less. They have postulated that the decrease in rotation is due to the adsorption of sugar by the colloidal particles and that the adsorbed sugar loses the property of rotating the plane of polarisation. By simple combustion experiments they have shown that the constituents of sugars are present in the coagula but they observed no optical rotation in solutions obtained by dissolving these coagula in proper solvents. These results have further been confirmed in a paper by Shrivastava, Gupta, Prasad and Bhatnagar (Journ. Phys. Chem., Feb. 1925). It has been definitely shown there that the optical inactivity of solutions of

coagula containing adsorbed sugar is not due to any other cause such as mutarotation but is due to a change in the nature of the sugar itself.

It becomes, therefore, interesting to see whether the observations of Zsigmondy and Bhatnagar and Shrivastava were peculiar to gelatine and sugars only or had a general application. In order, therefore, to obtain further evidence on the chemical theory of adsorption, the protection of colloidal solutions by soap solution was studied and the nature of adsorbed soap particles was in all cases examined.

EXPERIMENTAL.

The colloidal solutions used in the investigations were those of Arsenic hydrosulphide, Antimony hydrosulphide and Cadmium hydrosulphide. The colloidal solutions of Arsenic and Antimony hydrosulphides were prepared by dissolving Merck's pure Arsenious acid and Potassium Antimony tartrate, respectively, in freshly twice distilled water and then passing Hydrogen sulphide gas for some time. The excess of the gas was removed by passing a rapid current of Hydrogen gas through the solutions for about 24 hours until a sample of the sol produced no stain on lead acetate paper. The colloidal solution of Cadmium hydrosulphide was prepared by passing Hydrogen sulphide gas in an ammoniacal solution of Merck's pure Cadmium sulphate whereby Cadmium sulphide was precipitated. The precipitate was well washed on the filter paper until it was quite free from Ammonium Sulphate. It was then suspended in twice distilled water and Hydrogen sulphide gas was passed in, till a clear solution was obtained. The excess of the gas was removed by boiling the solution.

The soap solution, used, was that of Sodium oleate, which was prepared in the laboratory by the method

advocated by McBain. *Alcoholic solution of Sodium hydroxide was added gradually to an alcoholic solution of Oleic acid and the neutrality of the mixture was tested by Phenolphthalein. The soap was then dried till it was completely free from alcohol. The sample thus prepared had a melting point 232°-235°.

A solution of Sodium oleate was prepared by dissolving 5 grams of the soap in a litre of distilled water and solutions of other concentrations were obtained by diluting the original solution with water in varying proportions.

The investigation was accomplished by the use of Donnan's Drop pipette (Zeits. Phys. Chem., 31, 42, 1899) by means of which the number of drops in a given volume of the solution of soap were counted under standard conditions. The method of Drop numbers has been employed by Donnan and Potts (Koll. Zeit., 4, 208, 1910) in determining the emulsifying powers of alkalis. Lewis (Phil. Mag. 499, 1908) also used the same method in the study of adsorption of Sodium Glycoholate by the oil surface for the verification of the Gibbs-Thomson equation.

As the number of drops are greatly affected by the irregularities in the tip of the drop-pipette, it was carefully smoothed and necessary precautions were taken to keep it protected from grease or dust particles. The drop-pipette was cleaned with Potassium dichromate mixture and distilled water and was well dried before each observation.

* The number of drops in a fixed volume of solutions of soaps of various concentrations were first counted. A curve was then drawn with the concentration of soap solution as abscissa and the number of drops as ordinates as shown in Figure I. The variation in drop number with

change in concentration of soap' solution is brought out in the following table.

TABLE I.

No.	Concentration of soap solution.	Drop number.
1	0'0000%	240
2	0'0625%	568
3	0'1250%	617
4	0'1875%	624
5	0'2506%	631
6	0'3125%	638
7	0'3750%	645
8	0'4375%	652
9	0'5000%	659

It will be seen from the above table that Drop numbers increase with increase in concentration of the soap. As drop numbers are inversely proportional to surface tension as a first approximation, it shows that the surface tension of soap solutions continuously decreases as the concentration of the soap is increased.

The Drop numbers of the various colloidal solutions employed in the investigation were counted in the same volume as that of soap solutions and the results are shown in Table II.

TABLE II.

No.	Sols.	Drop number.
1	Arsenic Hydrosulphide	240
2	Antimony Hydrosulphide.	240
3	Cadmium Hydrosulphide.	240

The above table clearly shows that the colloidal particles do not take any part in altering the surface tension of the dispersing medium as the drop numbers for the three colloidal solutions examined are exactly the same as that of water (*cf.* Linder and Picton; Journ. Chem. Soc. '61, 111, 1892). This property of colloidal solution greatly facilitated the work as the addition of the colloidal solution to soap solution produced a simple dilution effect and the concentration of soap before adsorption could be easily calculated.

25 C. C. of the colloidal solutions were mixed with 25 C. C. of the soap solutions of different concentrations and were left for 24 hours. The number of drops in the same volume of the mixed solutions were then counted and the concentrations of the soap after adsorption were read off from the graph. The amount of soap adsorbed per 100 C.C. of the sol was then calculated and the values of x/m were obtained. The results of the investigation are shown in the following tables :—

TABLE III.

Soap used = Sodium oleate.
 Colloidal substance used = Arsenic hydrosulphide sol
 containing 0.8530 gram
 of AS_2S_3 per litre.

Original concentration of soap solution before mixing the sol.	Calculated concentration of soap in the mixed solution before adsorption.	Drop number of the mixture of sol and soap solution	Observed concentration of soap in the mixed solution after adsorption.	Amount of soap adsorbed per 100 C.C. of the sol.	x/m
0.5000%	0.2500%	595	0.0688%	0.3624 gms.	4.249
0.3750%	0.1875%	518	0.0500%	0.2750 ..	3.224
0.2500%	0.1250%	371	0.0250%	0.2000 ..	2.345
0.1250%	0.0625%	268	0.00688%	0.1124 ..	1.317

TABLE IV.

Soap used

= Sodium oleate.

Colloidal substance used = Antimony hydrosulphide
sol containing 0·3530
gram of Sb_2S_3 per litre.

Original concentration of soap solution before mixing the sol.	Calculated concentration of soap in the mixed solution before adsorption.	Drop number of the mixture of sol and soap solution.	Observed concentration of soap in the mixed solution after adsorption.	Amount of soap adsorbed per 100 C.C. of the sol.	x m
0·5000%	0·2500%	617	0·1250%	0·2500 gms	7·081
0·3750%	0·1875%	608	0·0875%	0·2000 "	5·665
0·2500%	0·1250%	588	0·0656%	0·1188 "	3·366
0·1250%	0·0625%	365	0·0250%	0·0750 "	0·212

TABLE V.

Soap used

= Sodium oleate.

Colloidal substance used = Cadmium sulphide hydro-sol.

Original concentration of soap solution before mixing the sol.	Calculated concentration of soap in the mixed solution before adsorption.	Drop number of the mixture of sol and soap solution.	Observed concentration of soap in the mixed solution after adsorption	Amount of soap adsorbed per 100 C.C. of the sol.
0·5000%	0·2500%	624	0·2000%	0·100 gms.
0·3750%	0·1875%	619	0·1438%	0·087 "
0·2500%	0·1250%	608	0·0875%	0·075 "
0·1250%	0·0625%	544	0·0568%	0·012 "

Some experiments were then performed with solid adsorbents. The fine precipitates employed were Merck's pure Zinc Oxide, Manganese Dioxide, Alumina, Red Lead, Fuller's earth, Barium Carbonate and Lead Chloride.

The particles of uniform sizes were separated by passing them through sieves of meshes of two successive

sizes (40 and 60 per inch). 50 C. C. of soap solutions of various concentrations were added to 5 grams of the precipitate and the mixtures were left for 24 hours. The soap solutions were then filtered and their concentrations were determined as described before by counting the number of drops in the given volume of the filtrate. To avoid any adsorption by filter papers during filtration, specially prepared filter papers were used. They were first soaked in soap solution of the same strength as added to the precipitates and were then dried after thorough washing. The results with various precipitates are shown in the following tables:—

TABLE VI.

Soap used = Sodium oleate.
Solid adsorbent used = Zinc Oxide.

Quantity of the solid. (m)	Original concen- tration of soap solution before mixing zinc oxide.	Drop number of the super- natant liquid.	Observed concen- tration of soap solution after adsorption. (c)	Amount of soap adsorbed by the solid. (x)	x/m
5 gms.	0.5000%	491	0.0469%	0.2265 gms.	0.0452
5 "	0.3750%	381	0.0250%	0.1750 "	0.0350
5 "	0.2500%	272	0.0063%	0.1218 "	0.0244
5 "	0.1250%	240	0.0000%	0.0625 "	0.0125

TABLE VII.

Soap used = Sodium oleate.
Solid adsorbent used = Manganese dioxide.

Quantity of the solid. (m)	Original concen- tration of soap solution before mixing manganese dioxide.	Drop number of the super- natant liquid.	Observed concen- tration of soap solution after adsorption. (c)	Amount of soap adsorbed by the solid. (x)	x/m
5 gms.	0.5000%	582	0.0656%	0.2172 gms.	0.0434
5 "	0.3750%	508	0.0500%	0.1625 "	0.0325
5 "	0.2500%	410	0.0312%	0.1094 "	0.0219
5 "	0.1250%	270	0.0064%	0.0593 "	0.0119

TABLE VIII.
Soap used = Sodium oleate.
Solid adsorbent used = Alumina.

Quantity of the solid. (n.)	Original concen- tration of soap solution before mixing Alumina.	Drop number of the superna- tient liquid.	Observed concen- tration of soap solution after adsorption. (c)	Amount of soap adsorbed by the solid. (x)	x m
5 gms.	0.5000%	620	0.1562%	0.1719 gms.	0.0344
5 "	0.3750%	596	0.0687%	0.1531 "	0.0306
5 "	0.2500%	555	0.0593%	0.0953 "	0.0191
5 "	0.1250%	340	0.0187%	0.0531	0.0106

TABLE IX.
Soap used = Sodium oleate.
Solid adsorbent used = Red Lead.

Quantity of the solid. (m)	Original concen- tration of soap solution before mixing Red lead.	Drop number of the superna- tient liquid.	Observed concen- tration of soap solution after adsorption. (c)	Amount of soap adsorbed by the solid. (x)	x m
5 gms.	0.5000%	578	0.0625%	0.2188 gms.	0.0438
5 "	0.3750%	578	0.0625%	0.1562 "	0.0312
5 "	0.2500%	578	0.0625%	0.0937 "	0.0187
5 "	0.1250%	550	0.0593	0.0820 "	0.0064

TABLE X.
Soap used = Sodium oleate.
Solid adsorbent used = Fuller's earth.

Quantity of the solid. (m)	Original concen- tration of soap solution before mixing Fuller's earth.	Drop number of the superna- tient liquid.	Observed concen- tration of soap solution after adsorption. (c)	Amount of soap adsorbed by the solid. (x)	x m
2 gms.	0.5000%	624	0.2000%	0.0150 gms.	0.0750
2 "	0.3750%	610	0.0875%	0.1437 "	0.0718
2 "	0.2500%	572	0.0625%	0.0937 "	0.0468
2 "	0.1250%	432	0.0375%	0.0437 "	0.0218

TABLE XI.

Soap used = Sodium oleate.
 Solid adsorbent used = Barium Carbonate.

Quantity of the solid. (m)	Original concen- tration of soap solution before mixing carbonate.	Drop number of the superna- tient liquid.	Observed concen- tration of soap solution after adsorption. (c)	Amount of soap adsorbed by the solid. (x)	x m
5 gms.	0.5600%	600	0.0719%	0.2140 gms.	0.0430
5 ..	0.3750%	592	0.0688%	0.1531 ..	0.0306
5 ..	0.2500%	584	0.0650%	0.0922 ..	0.0184
5 ..	0.1250%	549	0.0562%	0.0344 ..	0.0069

TABLE XII.

Soap used = Sodium oleate.
 Adsorbent used = Lead Chloride.

Quantity of the solid. (m)	Original concen- tration of soap solution before mixing lead chloride.	Drop number of the superna- tient liquid.	Observed concen- tration of soap solution after adsorption. (c)	Amount of soap adsorbed by the solid. (x)	x m
5 gms.	0.5000%	250	0.0081%	0.2484 gms.	0.0497
5 ..	0.3750%	246	0.0011%	0.1867 ..	0.0373
5 ..	0.2500%	242	0.0008%	0.1246 ..	0.0249
5 ..	0.1250%	240	0.0000%	0.0625 ..	0.0125

It will be seen from tables III-V that the observed concentration of the soap is not half as is expected on mixture law, but is in all cases less. The diminution in concentration is due to the adsorption of soap molecules by the particles of colloidal solutions which offer such a large surface (*cf.* Gibbs-Thomson equation). The same

conclusion can be drawn from the experiments made on fine powders. Also in each case the value of x/m have been calculated and the results indicate that the value of x/m decreases as the concentration of the soap is decreased. These observations clearly show that the phenomenon of protection is related to adsorption and precedes either an increase in the density of charge on the colloid particles or the formation of an envelope round them.

In order to see whether Freundlich's equation is applicable to these cases of adsorption, graphs with x/m and C , the end concentration, as co-ordinates were drawn. It was found that only in a few cases the $\log x/m$ and $\log C$ curves were straight lines (*cf. Prasad, Shrivastava and Gupta, "The mechanism of adsorption by colloidal solution and precipitate" communicated to Kolloid Zeitschrift*).

The state of the adsorbed soap was then examined by performing the following experiments :—

In the case of soap and sol system, the colloidal solution was coagulated by N/10 Barium Chloride and the coagula was well washed on the filter paper to remove the precipitating agent and the mechanically adhering soap molecules. As Whitney and Ober have shown (Journ. Amer. Chem. Soc., 23, 342, 1901), the above process does not remove any adsorbed substance. The coagula was then boiled in water for a long time and the numbers of the water so obtained were determined. Similarly fine powders were first well washed to remove any adhering soap molecules and then boiled in water for sufficient time. The drop numbers of this water were then counted as before. The results of only two cases are given in Tables XIII and XIV. Results obtained in case of other sols and precipitates were of the same nature.

TABLE XIII.

Soap used = Sodium oleate.

Colloidal substance used = Arsenic hydrosulphide sol containing 0·8580 gram of As_2S_3 per litre.

Original concentration of soap solution before mixing the sol.	Calculated concentration of soap in the mixed solution before adsorption.	Drop number of the mixture of sol and soap solution.	Observed concentration of soap in the mixed solution after adsorption. (c)	Amount of soap adsorbed per 100 C.C. of the sol. (x)	Drop number of the washings.
0·500%	0·2500%	595	0·0688 gms.	0·3624 gms.	240
0·375%	0·1875%	518	0·0500 ..	0·2750 ..	240
0·250%	0·1250%	371	0·0250 ..	0·2000 ..	240
0·125%	0·0625%	268	0·0363 ..	0·1125 ..	240

TABLE XIV.

Soap used = Sodium oleate.

Solid adsorbent used = Zinc oxide.

Quantity of the solid. (m)	Original concentration of soap solution before mixing Zinc oxide.	Drop number of the supernatent liquid.	Observed concentration of soap solution after adsorption. (c)	Amount of soap adsorbed by the solid. (x)	Drop number of the washings.
5 gms.	0·500%	491	0·0469%	0·2265 gms.	240
5 ..	0·375%	381	0·2500%	0·1750 ..	240
5 ..	0·250%	272	0·0668%	0·1218 ..	240
5 ..	0·125% •	240	0·0000%	0·0625 ..	• 240

The above observations clearly show that the adsorbed soap has lost its well known property of dissolving in water and lowering the surface tension and thus amply support the chemical theory of adsorption.

Further qualitative experiments were made to see the presence of the constituents of soap in the coagula and the precipitates.

The washed precipitate or coagulum was first dried in an air oven. It was then mixed with copper oxide and heated in a test-tube. The gas evolved was passed in lime water which became milky. A control experiment was done side by side with copper oxide and zinc oxide or any other precipitate. No milkiness of lime water was observed in any of the latter cases. These experiments show that the constituents of soaps are present in the precipitates and the coagula but do not exhibit their ordinary property of solution in water as they have undergone a radical change in the adsorbed state.

Some experiments were then made to study the adsorption of dyes by the fine precipitates. The method employed for the above investigation was the ordinary colorimetric method. The results of these experiments were also in the same direction as that of the soap solutions. The dye is adsorbed by the precipitates and loses its property of solubility in water in the adsorbed state.

These results clearly point out the advantage of using mordants in making a dye fast on a cloth. The mordants adsorb the dyes which in the adsorbed state undergo a vast change in the physical properties. They lose the property of solution in water in the adsorbed state and consequently the cloth remains unaffected by repeated washings.

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Travancore Essential Oils

Part VI.

From *Cymbopogon Caesius*; Stapf. (*Inchi Grass*).

By

KISHORI LAL MOUDGILL.

This grass grows wild in profusion on the dry hill-slopes of the Western Ghats in South Travancore, and is locally known as 'inchipul' (Ginger grass) because of the aroma given by the leaves and the flowers when they are rubbed. The shoots appear early after the rains in June and the grass flowers between October and January when it attains a height of 6 feet or more. At present it is not put to any use and is invariably destroyed by fire when it dries up.

The botanical identification of the grass presented several difficulties.² Ram Rao described the grass as *Andropogon schoenanthus*, Linn., and called it geranium grass (Flowering plants of Travancore) but Professor Rangachari of Coimbatore (*private report*) identified it as *Cymbopogon Caesius*, Stapf. This was subsequently confirmed by the Director of Kew Gardens and is in accord with the results of a detailed chemical examination, for, notwithstanding its aroma, the essential oil obtained from this grass by distillation with steam is quite different in character from the closely allied varieties, *Cymbopogon flexuous*, Stapf. (lemon grass) and *Cymbopogon Martini*,

¹ Lemon grass, *Cymbopogon flexuous*, Stapf is also known as 'inchipul.'

² It may be mentioned in this connection that much confusion, which was finally cleared by Stapf, had crept into the nomenclature of the grasses belonging to the family known as *Andropogon*.

Stapf.—formerly known as *Cymbopogon shoenanthus*, Linn., or *Andropogon shoenanthus*, Linn., or the 'motia' and 'sofia' grasses of Western India. Both these oils are well known in commerce, and citral and geraniol, the valuable constituents of the essential oils obtained from the former and the latter grasses respectively, are absent in this oil while borneol, which has not been reported in either of them, appears to be a characteristic constituent of the oil from 'inchi' grass.

A sample of the oil distilled from this grass was analysed at the request of the Department of Industries, Travancore, by Dr. Sudborough of the Indian Institute of Science and the Imperial Institute, London, and the latter reported that the oil might be employed as a substitute for palmarosa oil which it resembles in odour. An account of a preliminary work on this oil was published elsewhere (Moudgil and Krishna Iyer, Perfumery and Essential Oil Record, Vol. xiii, 1922, 292-295) and (Bulletin No. XVII, Department of Industries, Travancore). This paper describes the isolation and the identification of *l*-borneol, *l*-camphene, *l*-limonene and *l*-terpineol as some of the constituents of the oil. In view of the commercial possibilities suggested by the report of the Imperial Institute further work, reported below, was undertaken.

There are two varieties of the grass, one white and the other red. These two grow side by side in the same area and sometimes in the same cluster, and are not distinguishable from one another in odour or in any other respect except the colour of the stem and the base of the spikelets of the flowers, which in the case of the latter variety ranges from discoloured brown to red. The work described below was carried out mostly with the oil obtained from the white variety only, though the essential oils given by both of them as judged by their constants, are identical. (Table I.)

TABLE I.

		Red.	White.
$d_{4^{\circ}}^{28}$...	0·9130	0·9110
π_{D}^{28}	...	1·4820	1·4815
α_{D}^{30}	...	-3·60°	-40·0°
Acid value	..	Nil.	Nil.
Ester value	..	11·4	9·2
Ester value after acetylation.		121·8	117·4

N. B.—Both the varieties were cut from the same locality and at the same time.

It had been reported (Moudgill and Krishna Iyer, *loc. cit.*), that the difference in ester value caused by slight alterations in the conditions under which the estimation was carried out was due to the presence of terpineol but, in view of the isolation of a sesquiterpene alcohol which can be acetylated with great difficulty, this view has been modified. Consequently, the acetyl value can be used only to characterise the oil and does not afford much help in determining the proportions of alcohols present in the oil.

The constants of the oil obtained from the plant at different stages of its growth, as well as from different parts of the plant were determined. (Table II.) From these it would appear that the oil from the leaves distilled from the grass cut on different dates does not vary. The flowers yield a different oil and the characters of the oils from the upper third of the grass is to some extent modified after October, when the flowers appear, the alteration being most pronounced in February when the grass begins to dry up. The flowers give a larger yield of oil.

TABLE II.

Dates of distillation.	From the upper third of the plant only.						Leaves.		Flowers.
	5-6-22	10-7-22	13-8-22	12-9-22	12-10-22	13-12-22	6-2-22	6-2-22	-
Yield (dry) ...	3.75%	...	0.68%	0.78%	0.85%	0.65%	1.5%
$d_{4^\circ}^{28^\circ}$...	0.9070	0.9040	0.9020	0.9020	0.9030	0.9130	0.9130	0.9056	0.9388
n D ...	- 1.4840	1.4820	1.4826	1.4821	1.4845	1.4885	1.4910	1.4840	1.4921
Rotation ...	-38.0°	-36.8°	-37.5°	-32.8°	-32.0°	-32.5°	-37.5°	-42.5°	-22.9°
Acid value ...	1.1	0.9	1.0	0.7	1.6	1.8	1.8	0.4	0.4
Ester value ...	14.8	11.1	13.6	13.5	21.6	23.0	7.2	6.8	6.1
Acetyl value ...	93.5	97.0	104.0	117.2	96.0	...	89.0	100.0	78.0
Aldehydes per cent. ...	5.6	...	5.1	6.0	6.2	6.0	4.4	5.4	4.1

In view of the fact that several essential oils change on keeping, the constants of a sample of the oil were determined from time to time after storage for various periods in glass-stoppered bottles and in contact with anhydrous sodium sulphate. They indicate that the oil does not undergo any change, the little variations being well within the range of experimental error. (Table III.)

TABLE III.

Original oil.	After keeping for			
	3 months.	6 months.	10 months.	20 months.
Solubility in 70 per cent. alcohol.	insol.	insol.	insol.	insol.
Solubility in 80 per cent. alcohol.	7·0 vols.	7·2 vols.	7·2 vols.	7·2 vols.
Solubility in 87 per cent. alcohol.	0·8 vol.	1·0 vol.	0·9 vol.	1·0 vol.
d_{4}^{30}	0·9187	0·9176	0·9180	0·9178
Refractive index	1·484	1·4880	1·4883	1·4885
Optical rotation	-38·9	-37·5	-38·0	-34·0
Acid value	1·7	1·4	2·3	2·4
Ester value	5·6	6·0	6·0	7·1
Acetyl value	120·0	118·5	117·0	117·5

A more detailed examination of the oil has shown that, besides the constituent reported in an earlier paper (Moudgill and Krishna Iyer, *loc. cit.*), it contains a laevo-rotatory terpene alcohol which has not been obtained pure, a sesquiterpene and a liquid sesquiterpene alcohol, an aldehyde ($C_{10}H_{16}O$), and esters of acetic acid, butyric acid and an insoluble acid isomeric with oleic acid.

EXPERIMENTAL.

Fractionation.—An attempt has been made, with considerable success, to separate the oil into several fractions distilling over small ranges of temperature and to locate the major constituents of the oil by a comparative study of the changes in solubility in 80 per cent. and 90 per

cont'd alcohols, specific gravity and optical rotation, it being assumed that abrupt changes common to all the three properties would indicate a variation in the composition of the fraction. Fifteen hundred c.c. of the oil were fractionated under reduced pressure, first into three fractions and subsequently into twenty fractions (Table IV), each fraction in the latter case being collected over a range of 5 degrees. It would appear (see diagrams) that the oil consists of four chief fractions, each of which may consist of one or more than one constituent of the same class.

TABLE IV.

Fractions.	B.p.t.	Yield %.	Solubility in alcohol.			d_{4}^{29}	Specific rotation *
			80%	90%			
1	to 55°	7·5	insol.	7·2 vols.	0·8549		
2	-60°	5·6	"	4·8 "	0·8529	-69·25°	
3	-65°	5·9	"	8·0 "	0·8489	-75·78°	
4	-70°	3·6	"	4·8 "	0·8498	-70·15°	
5	-75°	8·8	"	3·6 "	0·8525	-69·98°	
6	-80°	1·7	"	5·1 "	0·8578	-65·30°	
7	-85°	2·2	"	4·2 "	0·8682		
8	-90°	1·4	7 vols.	all	0·9122	-51·46°	
9	-95°	1·7	1·2 "	"	0·8932	-40·46°	
10	-100°	1·9	0·9 "	"	0·9356	-34·05°	
11	-105°	2·8	0·9 "	"	0·9401	-32·73°	
12	-110°	8·4	0·9	"	0·9423	-31·25°	
13	-115°	2·0	0·85 "	"	0·9445	-32·43°	
14	-120°	6·3	0·85 "	"	0·9414	=28·24°	
15	-125°	2·7	insol.	0·2 vol.	0·9410	-19·95°	
16	-130°	2·2	"	all	0·9450	-15·43°	
17	-135°	1·7	"	"	0·9537	-13·02°	
18	-140°	5·6	"	all	0·9683	-9·99°	
19	-150°	6·3	1·2 vols.	"	0·9828	-0·55°	
20 †	-165°	6·6	0·9 "	"	0·9991	-0·00°	
Solid	...	4·2	
Loss and residue	...	15·0	

N.B.—The distillation was carried out under a pressure of 12-14 mm.

* The 19th and the 20th fraction boiled 10° higher than the previous fraction.

† The rotations were determined in 4 decimeter tubes, which alone were available at the time, in alcoholic solution, because, either the rotations of the homogeneous liquid were so high that they did not fall within the range of the polarimeter, or the specimens were so highly coloured that a column 4 decimeters long did not permit light to pass through. Smaller tubes were available in the latter part of the work.

1. *Fractions 1-8.*—Insoluble in 80 per cent. alcohol, soluble with difficulty in 90 per cent. alcohol, specific gravity 0·8500 to 0·8700, optical rotation -60° and above, consisting mainly of terpenes, camphene and limonene.

2. *Fractions 9-13.*—Soluble in equal volume of 80 per cent. alcohol, and in all proportions in 90 per cent. alcohol, specific gravity 0·8900 to 0·9400, optical rotation about -30° consisting mainly of alcohols, borneol, terpineol and another terpene alcohol which has not been isolated so far.

3. *Fractions 14-17.*—Insoluble in 80 per cent. alcohol, easily soluble in 90 per cent. alcohol, specific gravity about 0·9450. The abrupt change in the solubility curve (see diagrams, in 80 per cent. alcohol), indicates the presence of a compound sparingly soluble in alcohol. This was confirmed by the separation described below. The fractions were mixed and saponified with alcoholic caustic potash, the alkaline liquor being reserved for further work. The oil was dried over anhydrous sodium sulphate and distilled when the following fractions were obtained. (Table V.)

TABLE V.

No.	B.pt.	$d_{4^\circ}^{30^\circ}$	$n_D^{30^\circ}$	$\alpha_D^{28^\circ}$	Acetyl value.
1	220°-225° 760 mm.	0·9212	1·4800	...	197·3
2	225-230° 670 mm.	0·9224	1·4840	-22°	173·0
3	Up to 112°/16 mm.	0·9212	1·4928	-18·5°	110·0
4	" 115° "	0·9133	1·4930	-14·8°	42·5
5	" 123° "	0·9308	1·5025	-12·0°	115·3
6	" 135° "	0·9440	1·5063	-7·5°	...
7	" 155° "	0·9644	1·5098

The acetyl values of the different fractions indicate that No. 4 (b.pt. 112-115°/16 mm.) consists probably of a hydrocarbon. It was distilled repeatedly over sodium

and finally a nearly homogeneous colourless sesquiterpene ($C_{15}H_{24}$), which did not alter on repeated fractionation, was obtained $d_{4}^{30} 0.9064$, $n_D^{30} 1.5005$, $\alpha_D^{30} 12^\circ$

Found : C = 87.7 ; H = 11.2 per cent.

$C_{15}H_{24}$ requires C = 88.2 ; H = 11.8 per cent.

Unfortunately, only a small quantity of the oil was available for characterisation, and no solid derivative could be obtained. From a study of the molecular refraction and analysis of the liquid hydrobromide and dibromide (both unpurified), it appears that the hydrocarbon is a bicyclic sesquiterpene containing one double bond which is easily saturated. On treating it in glacial acetic acid solution in an ice-bath, with a cooled solution of bromine in the same solvent, nearly 1:1 molecules of bromine were absorbed for each molecule of the hydrocarbon. The *dibromide* was obtained as a liquid by pouring the above reaction mixture on ice and removing the oil by extraction with ether. The ethereal solution was dried over anhydrous sodium sulphate, the ether recovered and the oil kept in a vacuum desiccator for six weeks.

Found : Br = 41.37.

$C_{15}H_{24}Br_2$ requires Br = 43.15 per cent.

A liquid *monohydrobromide* was obtained in the usual way.

Found : Br = 30.58 per cent.

$C_{15}H_{25}Br$ requires Br = 28.07 per cent.

When the hydrocarbon was dissolved in acetone or acetic anhydride and the solution was treated with a trace of concentrated sulphuric acid, a green colouration was produced which turned blue on keeping. Solutions of the hydrocarbon in chloroform or glacial acetic acid, treated similarly, gave varying shades of purple.

Fraction 1-3 (Table V) were evidently mixtures of alcohols with the hydrocarbon. All attempts to obtain geraniol from these by treating with powdered calcium chloride in the cold and subsequent regeneration of the alcohol were unsuccessful. As they could not be purified further, their identity could not be established. Fractions 6 and 7 consist partly of a sesquiterpene alcohol and were added to the corresponding fractions below.

4. *Fractions 18 to 20.*—These were mixed and saponified with excess of alcoholic caustic potash, the alkaline extracts being reserved. Fractions 6 and 7 above (Table V) were mixed with the oil which was distilled and the following fractions obtained.

TABLE VI.

No.	B.pt. 16mm. pressure.	d_{10}^{30}	$" \frac{30}{D}$	Rotation.
1	135°-140°	0.9543	1.5040	-90°
2	140°-145°	0.9700	1.5090	-1.25°
3	145°-150°	0.9863	1.5108	+0°
4	150°-160°	0.9776	1.5092	+0°
5	Above 160°	0.9640	1.5090	+0°

The major portion of the oil distilled at 147°-149°/16 mm. and consisted of an optically inactive sesquiterpene alcohol ($C_{15}H_{26}O$). It would appear from the constants of fractions 4 and 5 that the alcohol undergoes decomposition on prolonged heating probably getting dehydrated and giving a lighter hydrocarbon. The alcohol cannot be acetylated easily. Under the normal conditions of acetylation, the acetyl value was 32, which corresponds to acetylation to the extent of only 13 per cent. In such cases, Boulez has recommended that a diluent with a low acetyl value should be employed and, if necessary, correction made to allow for the acetyl value of the diluent.

When acetylation was carried out in camphene solution and the period of heating with acetic anhydride prolonged, better results were obtained. Table VII gives the extent of acetylation under varying conditions of experiments. It appears that the alcohol is tertiary because the difficulties of acetylation met with in the case of this body are commonly experienced with tertiary alcohols.

TABLE VII.

Alcohol (4·6 parts) : camphene (25·6 parts).

Acetyl value of camphene = 6·0.

Duration of heating.	* 2 hrs.	4 hrs.	* 6 hrs.	8 hrs.	9 hrs.	11 hrs.
Ester value (found) ...	26·12	31·99	36·91	37·08	37·65	43·8
Corrected ...	20·12	25·99	30·91	31·08	31·65	37·8
% Acetylation in mixture ...	8·0	10·42	12·43	12·5	13·10	15·29
Acetylation for homogeneous liquid (calculated).	47·89	68·13	74·35	81·72	80·74	99·95

An attempt to prepare the benzoyl derivative by the Schotten-Baumann method proved equally unsuccessful, the resulting oil, changed in so far that it had a sweeter smell and different constants, gave an ester value of 63·2 which corresponds to benzoylation to the extent of 28 per cent. only. The alcohol is still under examination.

Treatment of the oil for isolating the aldehyde.—The oil is found to contain a small percentage of aldehyde (or ketone) at all stages of its growth. One litre of the oil was shaken repeatedly with a concentrated solution of sodium bisulphite, 100 cc. at a time. The extracts were mixed together, washed with ether ten times to remove traces of the adhering oil and warmed with excess of a solution of sodium carbonate when an oily layer separated. This was extracted with ether, the ethereal solution dried over anhydrous sodium sulphate and the

* The dilution in these two determinations was 4·7545 parts alcohol, 23·71 parts camphene.

ether removed. It was noticed that a portion of the oily layer did not dissolve in ether. On addition of some sodium chloride to the aqueous layer further quantities of this oil separated. It was removed with benzene, the benzene solution dried and the benzene recovered.

The sweet smelling oil recovered from the dry ethereal solution possessed the following constants. B.pt. 92°.

$94^\circ/4\cdot5 \text{ mm. } \alpha_{D}^{30^\circ} -6\cdot5^\circ, d_{4^\circ}^{30^\circ} 0\cdot9694, n_{D}^{30^\circ} 1\cdot4980.$

Found: C = 79·6; H = 9·7.

$\text{C}_{10}\text{H}_{14}\text{O}$ requires C = 80; H = 9·3 per cent.

$\text{C}_{10}\text{H}_{16}\text{O}$ requires C = 79·0; H = 10·5 per cent.

Preparation of the Semicarbazone.—A mixture of alcoholic solution of sodium acetate (1·3 grams) and semicarbazide hydrochloride (1·9 grams) was added to an alcoholic solution of the aldehyde (2·1 grams) and heated on a boiling water-bath during 30 minutes. It was allowed to stand for 24 hours and then poured into excess of water, when, on keeping for some hours, a semi-solid separated which was collected and drained on a porous plate. The solid thus obtained was crystallized from methyl alcohol, m.p. 170°-175°. The crystals were washed several times with anhydrous ether and the washings when evaporated deposited crystals, m.p. 164°. The residue was recrystallised from ethyl acetate, m.p. 181°. It would appear that the aldehyde extract obtained above contains two aldehydes, or, alternatively, the aldehyde in the mixture gives two semicarbazones, but owing to the scarcity of available material it was not possible to study this point further.

Attempts to prepare a solid oxime or a phenyl hydrazone were unsuccessful.

The benzene extract was found to solidify on keeping in a desiccator for a week. It is very hygroscopic and dissolves in water giving a colloidal solution from which it can be precipitated by adding concentrated aqueous solution of sodium chloride or any other inorganic salt. Attempts to crystallise it from organic solvents were unsuccessful. Qualitative analysis showed that the compound contained sodium and sulphur, and this and other characters of the solid suggested that a molecular compound of the aldehyde with sodium bisulphite had been obtained. This has been observed with several unsaturated aldehydes, most notably acraldehyde. The solid was purified as far as possible by dissolving it in water, precipitating with sodium chloride and extracting with benzene. Unfortunately, sufficient quantities for a complete analysis could not be obtained.

Found : Na = 5·4, 5·6 ; S = 8·78.

$(C_{10}H_{16}O)_2NaHSO_3$ requires Na = 5·63; S = 7·85 per cent.

The formula $(C_{10}H_{16}O)_2NaHSO_3$ has been deduced from the above results of analysis. In view of the discordant figure obtained for sulphur and the fact that the purity of the compound under analysis may be questioned, it is put forward tentatively and must be accepted with reserve.

Combined acids.—The alkaline extracts obtained after the saponification of the various fractions were mixed together, washed several times with ether to remove adherent oil and acidified with dilute sulphuric acid. An oil, smelling strongly of rancid butter, separated and was removed. The aqueous layer was neutralized with sodium hydroxide, reduced in bulk to about 200 cc., extracted again with ether, acidified with dilute sulphuric acid and distilled with steam. The volatile acids were collected in three fractions, converted into their silver salts and analysed.

Fraction 1. Found : Ag = 65·62. $C_2H_3O_2Ag$ requires Ag = 64·7 per cent.

Fraction 2. Found : Ag = 60·1 per cent.

Fraction 3. Found : Ag = 56·4. $C_4H_7O_2Ag$ requires Ag = 55·4 per cent.

Fractions 1 and 3 consist of acetic acid and butyric acid respectively. Even though the results of the silver salt obtained from fraction 2 would indicate the presence of propionic acid, it was neutralized, reduced in bulk, acidified and distilled with steam again. Three fractions were obtained and as the silver salts obtained from these did not give a figure for silver to correspond to silver propionate, fraction 2 was taken to have been a mixture of acetic acid and butyric acid.

The oily portion which had been removed with ether was repeatedly distilled with steam and finally obtained as a yellow oil smelling strongly of rancid fats. d_{4}^{30} 0·8732, n_{D}^{30} 1·4583. It was optically inactive, insoluble in water hot and cold, but readily soluble in all the common organic solvents. A suspension in water rapidly cleared when a dilute aqueous solution of caustic soda was added but after a moment the solution became turbid and gave a lather, characteristic of soaps. The silver salt prepared from an alcoholic solution of the oil was a white solid insoluble in water and very sparingly soluble in alcohol.

Found : Ag = 30·18, 29·40.

$C_{16}H_{31}O_2Ag$ requires Ag = 29·75 per cent.

$C_{16}H_{29}O_2Ag$, , Ag = 29·87 , ,

A solution of the acid in alcohol readily absorbs bromide. This fact and the high specific gravity and refractive index of the compound would point to its being

an unsaturated compound, because the values for the latter two increase, in the case of the acids containing the same number of carbon atoms, with the increase in the degree of unsaturation. The acid is probably an isomer of oleic acid with the formula $C_{16}H_{30}O_2$.

CONCLUSIONS.

1. *Cymbopogon Caesius*, Stapf. gives a sweet-smelling essential oil which is quite different in character from the oils obtained from similar grasses but resembles palmarosa oil in odour.
2. The oil occurs in the flowers and the leaves. The former yields more oil than the latter.
3. The oil does not undergo any change on storage.
4. The oil obtained from the leaves is fairly uniform during the different stages of the growth of the plant. The oil from the flower is richer in sesquiterpene constituents and has a much lower acetyl value than the oil from the leaves.
5. The constituents of the oil are:—*l*-limonene, *l*-camphene, *l*-borneol, *l*-terpeneol, a bicyclic sesquiterpene $d \frac{30}{4} 0.9064, n \frac{30}{4} 1.5005$, specific rotation at $\frac{D}{D} 30^{\circ} -12^{\circ}$, a tertiary sesquiterpene alcohol ($C_{15}H_{26}O$) and a terpene alcohol which could not be obtained in a pure state for characterisation. Besides these, the oil contains an aldehyde which gives a sodium salt of a sulphonic acid on treatment with sodium bisulphite, and esters of acetic acid, butyric acid, and an unsaturated acid $C_{16}H_{30}O_2$.
6. There are two varieties of the grass, one white and the other red, but they both give the same oil.

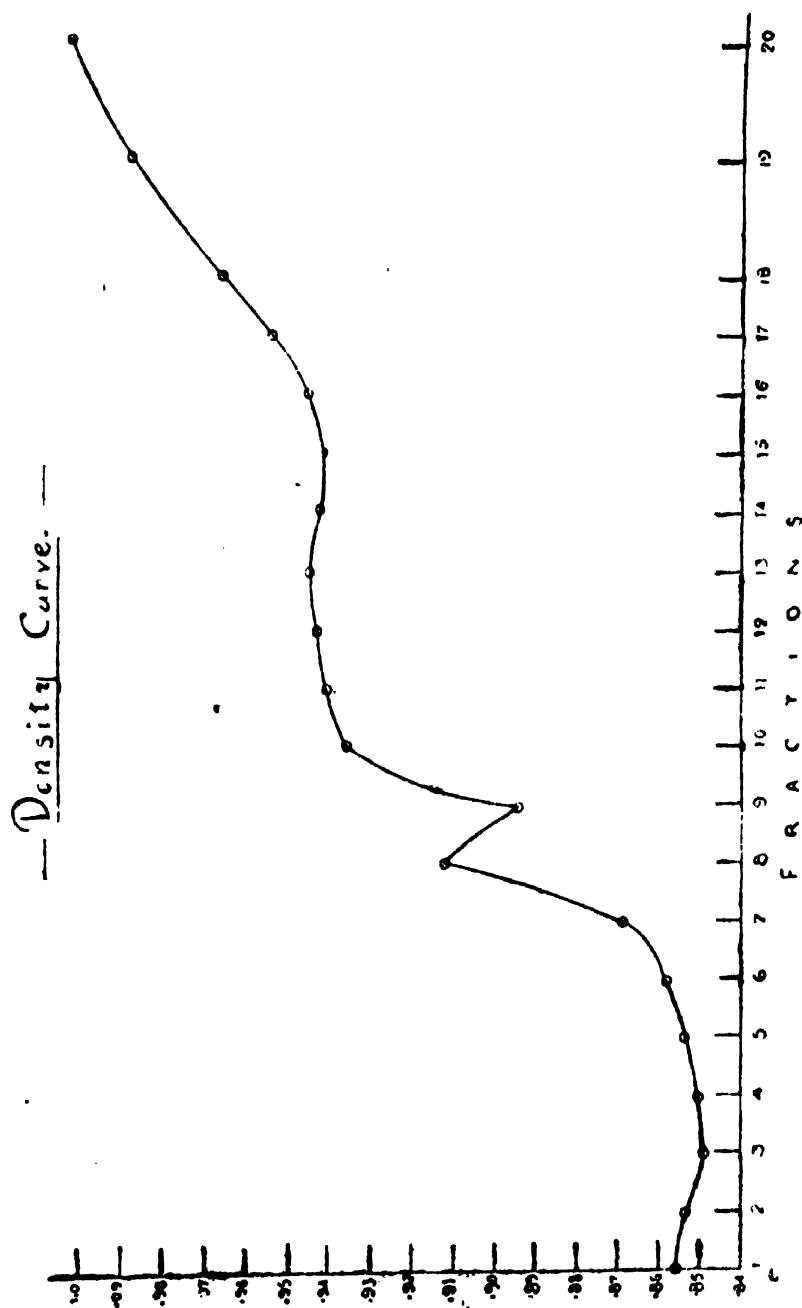
The work described in this paper was carried out mostly with the oil from the white variety.

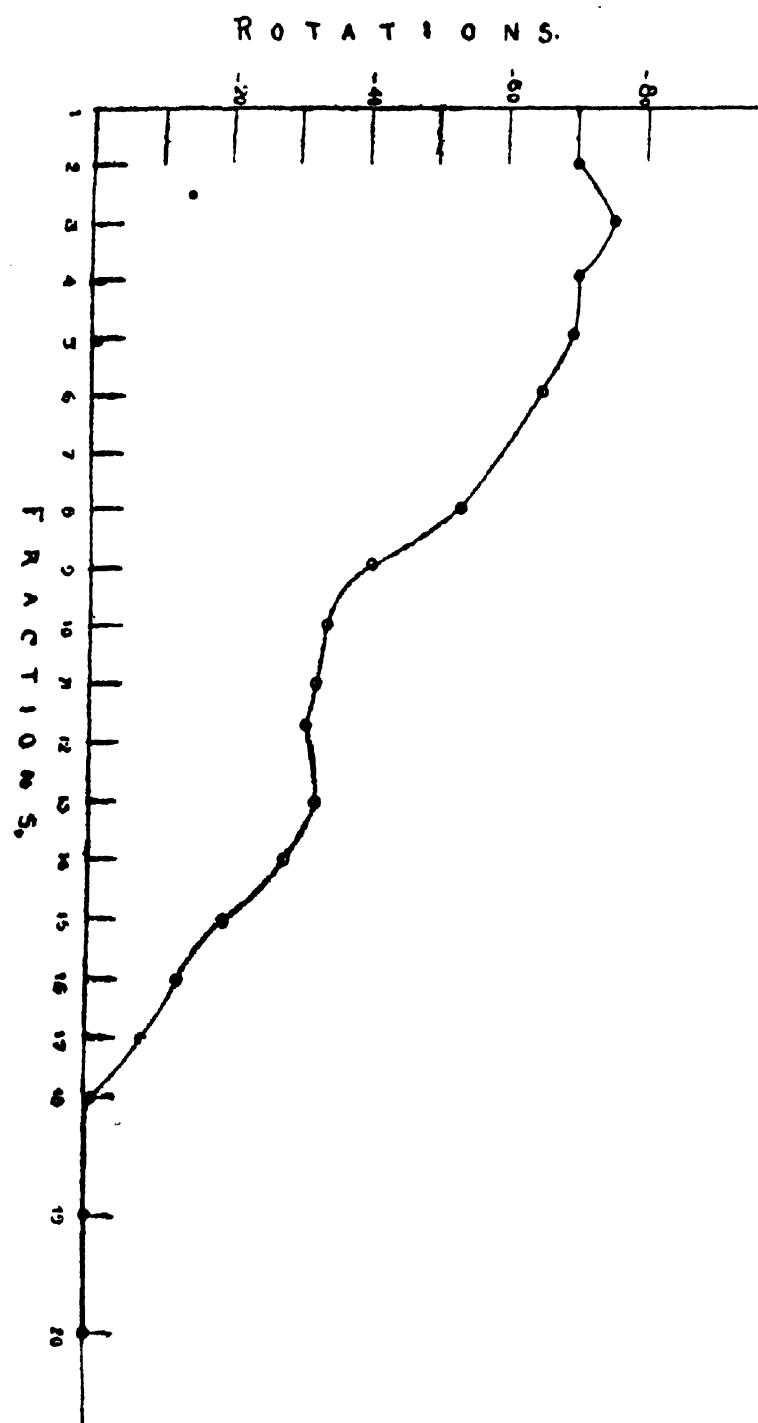
The author wishes to thank Mr. I. C. Chacko, the Director of Industries for affording facilities for the distillation of the oil. Thanks are due to Mr. K. R. Krishna Iyer, M.A., who collaborated in the preliminary stages of the work and to Mr. P. N. Vridhachalam for supervising the distillation of the grass.

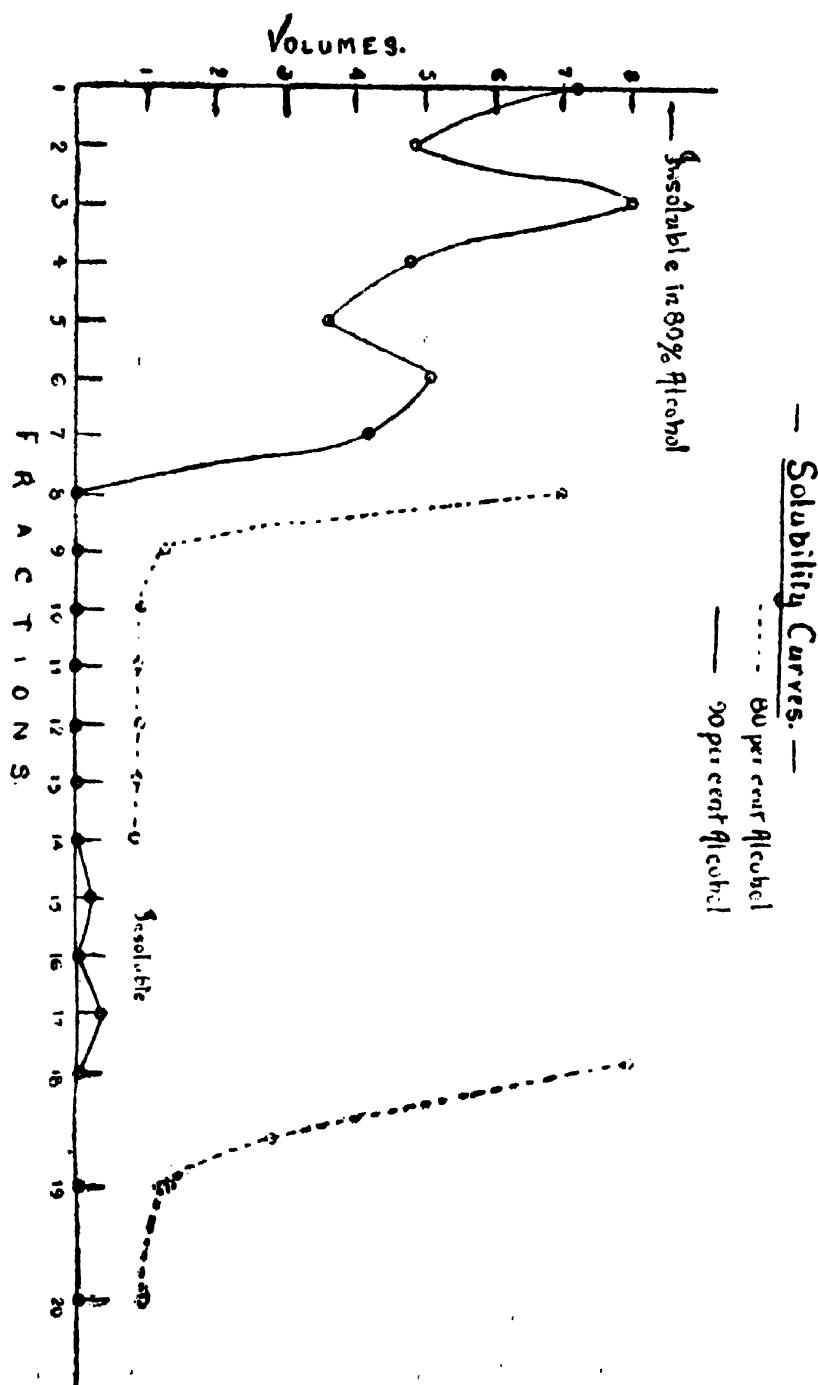
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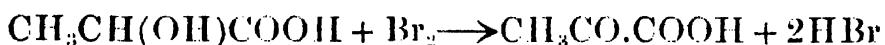


Bromination of Lactic Acid and Calcium Lactate in Presence of Light.

BY

JNANENDRA CHANDRA GHOSH AND KALIPADA BASU.

It is known already that bromine reacts with lactic acid in light (Ciusa and Piergallini, Atti R. Accad. Lincei, (5), 23, 237, 1914) to give pyruvic acid according to equation :



This investigation was begun with the object of finding out how the velocity constant of the photo-bromination varies with the intensity, frequency and the state of polarisation of incident light.

EXPERIMENT.

The experimental arrangement will be clear from Fig. 1.

The light-source L was a Point-o-lita arc lamp of 100 c. p. run from a battery maintained at 110 volts. C was a convex lens placed at a distance from the lamp equal to the focal length so as to obtain a parallel beam of light.

P is a water-filter, M is a Wratten monochromatic blue or green filter as the case may be. The reaction-vessel R was made of plane-parallel glass sides with a closed stopper at the top and was placed inside a double-jacketted copper box B with an opening on side. By continuous circulation of water through the copper box from

a thermostat by means of a pump, the temperature was maintained constant within 1°C .

Merck's chemically pure lactic acid was taken and made into $\frac{N}{10}$ solution. A deci-normal solution of bromine redistilled in the laboratory was prepared from time to time.

The rate of reaction was measured iodometrically by taking out 2 cc. of the solution from the reaction vessel at different intervals of time after exposure to light. Redistilled water was used throughout the experiments.

The results obtained in the case of photo-bromination of lactic acid were somewhat irregular and Tables I, II and III show the best results obtained.

TABLE I.

Temperature— $35\cdot0^{\circ}$. Wave-length limit : $490-530\mu\mu$.

Initial concentration of bromine $\frac{N}{30}$.

Initial concentration of lactic acid $\frac{N}{30}$.

Time in mins.	Concentration of bromine $\frac{N}{100}$	Monomolecular velocity-constants.
0	5·55 c.c.	...
25	5·0	·00181
75	4·1	·00175
125	3·25	·00186
177	2·1	·00235

TABLE II.

Temp. 35°C. Wave-length limit : 440 - 500 $\mu\mu$.Concentration of bromine $\frac{N}{30}$.Initial concentration of lactic acid $\frac{N}{30}$.

Time in mins.	Concentration of bromine $\frac{N}{30}$	Monomolecular velocity- constants.
0	4.9 c.c.	...
25	4.3	.00227
75	3.45	.00203
101	2.25	.00210
136	1.95	.00204

TABLE III.

Temp. 35°C. Dark reaction.

Initial composition of the solution : same as in Tables I and II.

Time in mins.	Concentration of bromine $\frac{N}{100}$	Monomolecular velocity- constants.
0	5.8 c.c.	...
30	5.25	.00135
64	4.75	.00137
94	4.5	.00117
150	4.1	.00100

It is thus clear that there is a considerable dark reaction which accounts for about $\frac{2}{3}$ of the observed reaction.

The photo-chemical efficiency of light is not thus capable of very exact measurement as the velocity of pure photo-chemical reaction is always the difference between the observed light reaction and the dark reaction.

The idea of measuring the velocity of reaction for the same intensity of plane polarised and circularly polarised light was, therefore, abandoned, as the results that would be obtained in those cases could never be considered very trustworthy.

Application of Einstein's Law of Photo-chemical Equivalence.

The intensity of the radiations was measured by a thermopile with a low resistance sensitive galvanometer by comparison with a standard Heffner lamp and was found for blue light to be 13×900 ergs per sq. cm. per sec. and for green light 12.7×900 ergs sq. cm. per sec.

Number of gm. mole of bromine transformed by absorbed light per sec. per sq. cm. of surface \times the depth of the reaction vessel (2.5 cm.) :—

Taking the results of Table I where the change is .55 c.c. $\frac{N}{100}$ in 2 c.c. of the solution in the first 25 minutes and remembering that only one-third of the total reaction velocity is due to absorption of light, the above comes out to be

$$\begin{aligned} & \frac{1}{3} \times \frac{.0055}{2 \times 2} \times \frac{1}{25 \times 60} \times \frac{1}{1000} \times 2.5 \text{ gm. mols. per sec.} \\ & = 7.6 \times 10^{-10} \text{ gm. mols. per sec.} \\ & = 7.6 \times 10^{-10} \times 6.1 \times 10^{23} \text{ mols. per sec.} \\ & = 46.4 \times 10^{-13} \text{ mols. per sec.} \end{aligned}$$

Now, according to Noddak 70% of the incident blue or green light is absorbed by the bromine solution and thus the energy absorbed per sq. cm. per sec. is $13 \times 900 \times .7$ ergs. the frequency of the energy employed $\frac{3 \times 10^{10}}{500 \times 10^{-7}}$.

Hence the number of quanta of energy absorbed

$$= 13 \times 900 \times 7 \times \frac{500 \times 10^{-7}}{3 \times 10^{16}} \times \frac{1}{6.5 \times 10^{-27}}$$

$$= 210 \times 10^{13}$$

Four quanta of energy, therefore, activated one molecule of bromine and Einstein's law of photochemical equivalence appears not to hold here.

Bromination of Calcium Lactate.

The bromination of lactic acid sometimes gave irregular results and it was apprehended that the lactic acid used might not have been absolutely pure. A pure salt of lactic acid was, therefore, tried and calcium lactate was selected as it is easy to purify by repeated crystallisations.

Experimental data are given in Tables IV and V.

TABLE IV.

Temp. 35°C. Wave-length limit : 490-530 $\mu\mu$.

Initial conc. of bromine $\frac{N}{30}$.

Initial conc. of calcium lactate $\frac{N}{30}$.

Time in mins.	Concentration of bromine $\frac{N}{100}$.	Monomolecular velocity constants.
0	6.45.e.e.	...
24	4.65	.00592
48	3.35	.00593
72	2.35	.00609
96	1.65	.00617

TABLE V.

Temp. 35°C. Wave-length limit: 490-530 $\mu\mu$.

Initial concentration of bromine $\frac{N}{15}$.

Initial concentration of calcium lactate $\frac{N}{30}$.

Time in mins.	Concentration of bromine $\frac{N}{100}$	Monomolecular velocity constants.
0	11.35	...
10	9.80	.00638
20	8.35	.00661
30	6.95	.00710
40	5.55	.00770

Table IV indicates that the reaction is monomolecular. If the initial concentration of calcium lactate be raised to $\frac{N}{15}$, keeping the bromine concentration constant, the velocity constant increases to .00925 and very good constants are obtained at this concentration as well.

Table VI gives the velocity-constants for increased concentration of calcium lactate.

TABLE VI.

Temperature 35°C. Wave-length limit: 490-530 $\mu\mu$.

Initial concentration of bromine $\frac{N}{30}$.

Initial concentration of calcium lactate $\frac{N}{15}$.

Time in mins.	Concentration of bromine $\frac{N}{100}$	Monomolecular velocity constants.
0	6.15 c.c.	...
12	4.7	.00935
29	3.35	.00910
44	2.35	.00927
59	1.75	.00925

Such result is indeed to be expected. Bromine is here the photo-active molecule. It gets excited by absorption of light and if within its life-period of excitation it collides with an acceptor calcium lactate molecule reaction will take place. The velocity of reaction should necessarily be greater, the greater the concentration of acceptor molecule and will reach a maximum limit when the concentration of the acceptor molecule is so high that all the activated bromine molecules will have an opportunity of colliding with calcium lactate molecules within its life-period of excitation.

Increase in the concentration of bromine makes the velocity constant irregular as will be apparent from Table V. The reaction tends to degenerate into a zero molecular one. If we assume that the velocity of reaction is essentially governed by the rate of production of excited bromine molecules then

$$\frac{dx}{dt} = kI_0 \left(1 - e^{-\epsilon C} \right)$$

where I_0 is the intensity of incident light and ϵ the extinction co-efficient of bromine. For small values of C ,

$$\frac{dx}{dt} = kI_0 \left[1 - e^{-\epsilon C} \right]$$

$$= kI_0 \epsilon C$$

Hence the reaction is monomolecular. For large values of C , $e^{-\epsilon C}$ is negligibly small and $\frac{dx}{dt} = kI_0$, i.e., the reaction is zero-molecular.

TABLE VII.
Temperature 35·0°C.
Wave-length : 440-500 $\mu\mu$.

Initial cone. of Br.	Initial con. of cal. lactate.	Monomolecular velocity constants.
N 30	N 30	.00633
N 30	N 15	.00947
N 15	N 30	.00660—.00792 *

* The velocity constants are irregular and the reaction tends to become a zero-molecular one.

TABLE VIII.
Temperature 35°C.
Initial concentration of Br. N
30.

Initial concentration of calcium lactate N
30.

Dark Reaction.

Time in mins.	Concentration of bromine N 100.	Monomolecular velocity constants.
0	6·15 c.c.	...
20	4·95	" .00472
41	4·10	.00467
60	3·20	.00472
92	2·30	.00464

Velocity of Dark Reaction.—Table VIII gives the velocity of dark reaction at 35°C. It will be seen from comparison with Table IV that about $\frac{3}{4}$ of the velocity constant is due to dark reaction. It is curious that the dark reaction where the concentration of the reacting molecules of bromine and of calcium lactate are comparable should give a mono-molecular velocity constant and not a bimolecular one.

Application of Einstein's Law.

Number of quanta of energy absorbed = 21.7×10^{14} .

A. For calcium lactate concentration $\dots \frac{N}{30}$.

Number of gm. mols. transformed by light per second per sq. cm. \times depth of reaction vessel, taking the results of Table IV.

$$\frac{1}{4} \times \frac{.018}{2 \times 2} \times \frac{1}{24 \times 60} \times \frac{1}{1000} \times 2.5 \text{ gm. mols.}$$

$$= 20 \times 10^{-10} \text{ gm. mols.}$$

$$= 12.6 \times 10^{14} \text{ molecules.}$$

[One-fourth of the observed velocity in this case being due to light, *vide* Tables IV and VIII.]

B. For calcium lactate concentration $\dots \frac{N}{15}$.

Number of gm. mols. transformed by light per sec. per sq. cm. \times depth of reaction vessel, taking the results of Table VI.

$$\frac{1}{4} \times \frac{.0145}{2 \times 2} \times \frac{1}{12 \times 60} \times \frac{1}{1000} \times 2.5 \text{ gm. mols.}$$

$$= .333 \times 10^{-8} \text{ gm. mols.}$$

$$= .333 \times 10^{-8} \times 6.1 \times 10^{25} \text{ molecules}$$

$$= 20.31 \times 10^{14} \text{ molecules.}$$

We thus find that when the concentration of acceptor molecule of calcium lactate is small, *viz.*, $\frac{N}{30}$, about two quanta is necessary for the transformation of one molecule of calcium lactate. But as the concentration of calcium lactate is increased to $\frac{N}{15}$, about one quantum is necessary for the transformation of one molecule of calcium lactate.

This result is in agreement with the observation of Noddak (Zeit. für Electrochemie, 1921, 27, 359) who showed that as the concentration of CCl_3Br in CCl_4 is diminished, the photo-chemical efficiency of the chlorination process diminishes as given in the Table IX enclosed.

TABLE IX.

Dilution $\text{CCl}_3\text{Br} : \text{CCl}_4$	Br. liberated as observed : Br. change as calculated from Einstein's Law.
1 : 2	.90
1 : 16	.39
1 : 64	.071

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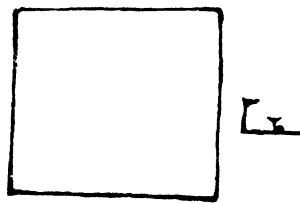
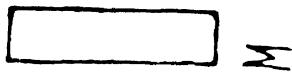
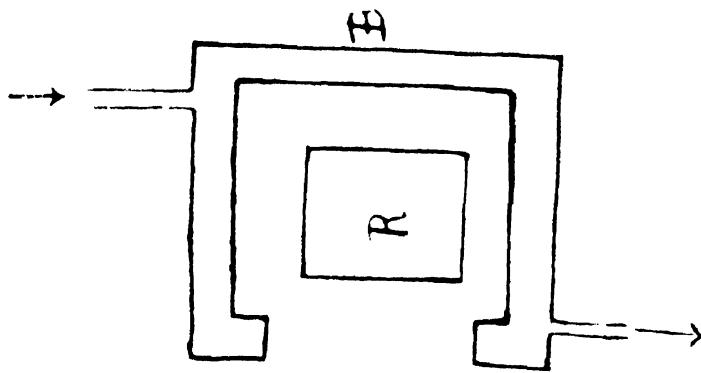
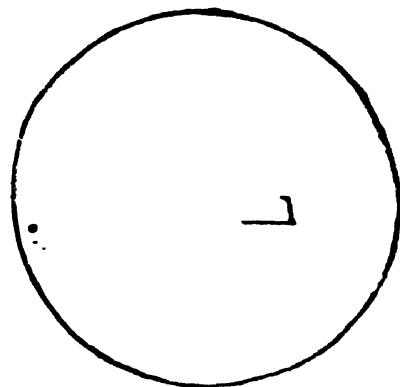


Fig. I



The Phase Rule and its Application to Problems of Luminescence and Ionisation of Gases.

By

MEGHNAJ SAHA.

The phase rule was discovered by the great American physicist, Willard Gibbs, in the year 1877, but was first popularised by W. Ostwald in the year 1894, in his *Wissenschaftliche Klassiker*. Since this date, it has formed one of the corner-stones of the science of physical chemistry, and has served as an invaluable guide for the study of problems of gaseous equilibrium, and changes of state.

The present author has shown about four years ago that a thermal stimulus alone can excite atoms to luminescence and ionisation, and how these problems can be treated thermodynamically. A serious defect of these theories is that radiation which plays an essential part in determining the equilibrium cannot be taken into account. The theory has been extended by Russell in America,² Darwin, Fowler and Milne³ in England and by Enskog⁴ and Becker⁵ in Germany. But though many

¹ M. N. Saha, On a Physical Theory of Stellar Spectra, Proc. Roy. Soc., Lond. 1921), Vol. 99, p. 135

² H. N. Russell, The Astrophysical Journal, Vol. 55, pp. 119-144.

³ C. G. Darwin and R. H. Fowler, The Philosophical Magazine, Vol. 45, page 1. 1924.

⁴ R. H. Fowler and E. A. Milne, Proc. Phys. Soc., London, Vol. 35, p. 94.

essential improvements have been made, none of the attempts to include radiation as a factor in determining the equilibrium can be said to have met with success.

The object of the present paper is to present the ionisation theory from the standpoint of the phase rule. The phase rule states that if in a gaseous system C = number of independent components, P = number of phases, F = number of degrees of freedom, then

$$F = C + 2 - P \quad \dots \quad (1)$$

Case 1. Take Ca-metal which is heated in a closed vessel. We neglect the intermediate stages, and consider simply the equilibrium



the neutral atoms directly dissociating into the positively charged atom and the electron. We suppose that the vessel emits no electrons.

Here we have C = 1, because the concentration of electrons is determined by the fraction x of original Ca-atoms ionised. P = 1 (all are in the gaseous phase). Variables—T, p , and x (fraction ionised). From the phase rule,

$$F = 1 + 2 - 1 = 2,$$

i.e., when 2 variables are given, say T and p , the third, x , is automatically determined. The equation connecting x , T and P is the well known law of ionisation.

$$\log \frac{x^2}{1-x^2} \cdot P' = -\frac{U}{2.3RT} + \frac{5}{2} \log T - 6.5 \quad \dots \quad (3)$$

Case 2. Ionisation of calcium gas in an atmosphere containing an excess of electrons.

This is a two component system, the independent components being Ca^+ (concentration y), e (concentration x), Ca-atoms may be regarded as a compound of Ca^+ and e . The variables are now T , p , x and y .

Consequently, $F = C + 2 - p = 3$.

Now we have four variables, and the number of degrees of freedom 3. Hence there must be one equation connecting the variables T , p , x , and y . This is the equation first given by Russell.

$$\log \frac{P_{\text{Ca}^+} P_e}{P_{\text{Ca}}} = K \quad \dots \quad (4)$$

P_{Ca^+} = partial pressure due to Ca^+ atoms,

P_e = partial pressure of electrons, etc.,

Now,

$$P_{\text{Ca}^+} = yRT, \quad P_e = xRT, \quad P_{\text{Ca}} = (1-y)RT$$

$$P = P_{\text{Ca}^+} + P_e + P_{\text{Ca}} = (1+x)RT.$$

Hence

$$P_{\text{Ca}^+} = \frac{y}{1+x} P, \quad P_e = \frac{x}{1+x} P, \quad P_{\text{Ca}} = \frac{1-y}{1+x} P,$$

Thus

$$\log \frac{x}{1+x} \cdot \frac{y}{1-y} p = - \frac{U}{2.3 RT} + \frac{5}{2} \log T - 6.5 \quad \dots \quad (4')$$

where U = heat of ionisation.

Case 3. Double Ionisation.

"Let us now treat the case when calcium vapour is heated within an enclosure to such a temperature, that not only is calcium ionised to Ca^+ and e , but some fraction of Ca^+ is also ionised to Ca^{++} and e .

The reactions are now



taking place simultaneously from Ca-vapour alone. This is a one component system, because the products, if all reduced to absolute zero, would yield only Ca-atoms leaving no excess of electrons.

The variables are T , p , x and y , where x , fraction of atoms ionised to Ca^+ and y , fraction ionised to Ca^{++} . There is only one phase. From the phase rule,

$$F = 1 + 2 - 1 = 2.$$

There are four variables, but the number of degrees of freedom is two. Hence we must have two independent equations. These are the equations of mass action representing the two reactions.



We have

$$\log \frac{P_{\text{Ca}^+} P_e}{P_{\text{Ca}}} = K, \quad \log \frac{P_{\text{Ca}^{++}} P_e}{P_{\text{Ca}}} = K' \quad \dots \quad (6)$$

Now

$$P_{\text{Ca}} = (1-x-y)RT, \quad P_{\text{Ca}^+} = xRT, \quad P_{\text{Ca}^{++}} = yRT$$

$$P_e = (x+2y)RT \text{ and hence } P = (1+x-2y)RT$$

Hence

$$\log \frac{x(x+2y)}{(1+x+2y)(1-x-y)} P = -\frac{U_1}{2.3RT} + \frac{5}{2} \log T - 6.5. \dots (6')$$

$$\log \frac{y(x+2y)}{x(1+x+2y)} P = -\frac{U_2}{2.3RT} + \frac{5}{2} \log T - 6.5 \dots (6'')$$

since P and T are given, x and y are perfectly determinate.

Case 4. Double ionisation, but concentration of electrons is now arbitrary.

The variables are now T, P, x, y and f , where

x = fraction of Ca atoms ionised to Ca^+

y = , , , , Ca^{++}

f = concentration of electrons
concentration of original Ca atoms.

The number of independent components is now two, for if the system be reduced to absolute zero, we shall be left with Ca atoms and an excess of electrons.

Phase = 1 (gaseous).

Hence from the phase rule

$$F = C + 2 - P = 3.$$

We have five variables, but the number of degrees of freedom is 3. Hence we must have two independent equations. These are the equations of mass action representing the reactions



The equations now take the forms:

$$\log \frac{x}{1-x-y} \cdot \frac{f}{1+f} = K = -\frac{U_1}{2.3RT} + \frac{5}{2} \log T - 6.5$$

$$\log \frac{y}{x} + \frac{f}{1+f} = K' = -\frac{U_2}{2.3RT} + \frac{5}{2} \log T - 6.5 \quad \dots \quad (7)$$

U_1 and U_2 = heats of first stage and second stage ionisation respectively.

From these two equations, it will appear that x and y cannot be determined unless f is known. This fact may have an interesting application in the problem of successive disappearance of lines of Si, Si^+ , Si^{++} and Si^{+++} in stars, because in high temperature stars, f must be abnormally high, and we may put

$$\frac{f}{1+f} = 1$$

For treble ionisation in an atmosphere of excess of electrons, the equations will take the form

$$\log \frac{x}{1-x-y-z} \cdot \frac{f}{1+f} = K_v$$

$$\log \frac{y}{x} \cdot \frac{f}{1-f} = K, \quad \dots \quad (8)$$

$$\log \frac{z}{y} \cdot \frac{f}{1+f} = K_s.$$

If we change the notation a little, we can express the formula in a symmetrical form. Let $x_0, x_1, x_2, x_3, \dots, x_n$ denote the fraction of Ca atoms which are respectively neutral, singly ionised, doubly ionised, etc.

then $x_0 + x_1 + x_2 + x_3 + \dots = 1$

and let f denote the ratio concentration of electrons to the original number of Ca atoms.

then we have

$$\log \frac{x_1}{x_0}, \frac{f}{1+f} = K_1$$

$$\log \frac{x_2}{x_1}, \frac{f}{1+f} = K_2$$

$$\log \frac{x_3}{x_2}, \frac{f}{1+f} = K_3$$

(8')

It is clear that the method might be extended to cover such cases as the reaction of any positively charged particle with any negatively charged particle which need not necessarily be an electron. We have been assuming so far that an ionised metal ion, say Ca^+ , can only combine with an electron, but there is no reason why Ca^+ will not combine with a negatively charged atom like Cl or O, giving us a $\text{Ca}^+ \text{Cl}^-$ or $\text{Ca}^+ \text{O}^-$ molecule having its characteristic band spectrum. The Cl ion will be as likely to combine with a positively charged particle as a free electron. But as we know nothing about the spectroscopy of such processes, no purpose will be served by putting down the equations. The suggestion is thrown here simply to account for the non-recurrence of the lines of electronegative gases like Cl, Br and I in the solar spectrum, and for the occurrence of a large number of lines showing a band structure, e.g., the bands ascribed to CN.

Radiation as a factor in determining the equilibrium.

As has been pointed out on several previous occasions, radiation must play a very essential rôle in determining the equilibrium. For there are an infinite number of

metastable quantum orbits between the normal state and the ionised state. In passing from the normal to the ionised state, the atom may pass through these states. As radiation pours through the normal atom, the pulses belonging to the principal series are absorbed, and the atom passes to the metastable state. It is easier to ionise the metastable states, e.g., in the case of a sodium atom in the $2p$ stage, the ionisation potential is 2.6 volts. The percentage of ionised Na atoms will therefore be materially affected by the density of radiant energy in the space corresponding to the characteristic lines of Na.

It is evident from the above that in addition to considering reactions of the type



we have also to consider such reactions as



i.e., radiation ν_{1s-2p} enters into the equilibrium. These are quite new types, and I have yet no clear idea how to tackle these problems. Yet a few casual remarks may be made.

Smit expresses the opinion that in the analogous case of photo-chemical equilibrium, besides T and p , the intensity of light will also appear as a new variable. The phase rule must then be modified from the form

$$F = C + 2 - P \text{ to the form } F = C + 3 - P$$

But no theoretical argument is given. We may regard Na_{2p} as a new component, if excess of ν_{1s-2p} pulses

be present. There is no objection in calling Na_{2p} or any other excited state of Na as a new component, because the ionisation potential, consequently the chemical properties of the excited atom are widely different from those of the normal atom. We have then from $F=C+2-P$, since $C=2$ and $P=1$, $F=3$ or the number of degrees of freedom is three, T , p , and the intensity of light. The cases can now be subdivided into two broad categories:—(1) Cases in which we start with Na atoms only, and the proportion Na_{2p} , or the $h\nu_{1s-2p}$ pulses is determined by the value T and p only. We may say that in such cases, the radiation is in equilibrium with matter at this temperature. (2) Cases in which Na atoms, otherwise all in the (1s) orbit, are illuminated by (1s-2p) pulses. The proportion of Na_{2p} atoms will now be completely determined by the intensity of (1s-2p) pulses. To this class belong the various absorption experiments performed by Wood, Bevan and others. (3) Classes intermediate between the two, e.g., the solar chromosphere, where T is sufficiently high to convert Na_{1s} atoms to Na_{2p} states, but in addition, there are the 1s-2p pulses pouring from the photosphere. Here the equilibrium will depend upon T , p and the intensity of light. That the chromosphere is not in a state of thermodynamic equilibrium was first pointed out by E. A. Milne in a recent letter to *Nature*.

It is evident that instead of Na_{2p} atoms, the reacting pulse of light $\nu=1s-2p$ may be looked upon as a new component.

⁸ Enskog, *Annalen der Physik*, Band 72.

⁹ R. Becker, *Zeitschrift für Physik*, B 18, 325, Vol. 28, p. 258.

⁷ H. N. Russell, *loc. cit.*, p. 144.

⁸ Pringsheim, *Physik der Sonne*, p. 3.

⁹ Smits, *The Theory of Allotropy* Transl. VII, p. 177.

The range within which a particular state may occur.

In this connection it is necessary to add a few words regarding the thermodynamical range within which a particular metastable state may occur. To introduce the matter we may begin with a general examination of the effect of heat on matter. The states succeeding each other may be visualized in the following scheme given by me a few years ago.

HYDROGEN.

State.	Phenomena.
Solid.	Fusion.
↓ Liquid.	Vaporisation.
↓ Gas (molecular)	Dissociation.
↓ Atomic state.	Luminescence.
↓ Excited states of atoms.	Ionisation.
↓ Positively charged atom.	

It does not always follow that the succeeding stages occur in the order given above. Thus, to take a familiar example, camphor vaporises directly without melting at all. Water can be obtained in the liquid form between 0°C and 100°C under the conditions prevailing in this globe of ours, but if the experimenter is transported to the moon, where the vapour is, say only 2 mms. of mercury, ice would behave just like camphor and vaporise without melting at all. The experimenter

on the moon would have to increase the pressure artificially to get the liquid stage. A similar case is that of carbon which vaporises without previously melting but Lummer and others¹ claim that they have obtained the liquid stage by heating carbon under great pressure.

The analogy may be extended further. In the cases of tungsten, platinum and other metals, the metal emits electrons even in the solid state.

The problem we are discussing here is the range of experimental conditions in temperature and pressure, within which a metastable state, say $2p$ or $3d$ of sodium or any other element may occur. It has been recorded by several observers that it is very difficult to obtain the exact experimental conditions at which the $2p$ or $3d$ orbits would occur in sufficient proportion to give us the diffuse and the sharp lines in absorption. At low temperatures the stimulus is not sufficient to produce an appreciable number of Na_{2p} atoms. If the temperature be sufficiently raised, they pass directly into ionised condition. The intermediate states may be obtained by combining high temperature with high pressure, or using a very long column of vapour at comparatively low temperature and low pressure. A similar phenomenon is well known to spectroscopists in the case of the spectra of C and Si. The ionised spectra of these elements have been studied in great detail, but it is very difficult to get lines of the neutral atoms. Only a few lines are recorded.² Probably when carbon and silicon vaporise directly from the solid state, a large percentage of them are ionised or there is not much range for the metastable states of C or Si to be developed. Even when the spectra

¹ Kohn—Zeitschrift für Physik, Vol. 27 (1924), p. 305.

² T. R. Merton and R. C. Johnson, Proc. Roy. Soc., London, Vol. 103, p. 394.

are obtained from vacuum discharge through their volatile compounds, they split more readily into C⁺ or C⁺⁺ than into the neutral form. Attempts are being made to study these phenomena experimentally.

The author had many opportunities of discussing the subject-matter (from the standpoint of the physical chemist) with his friend Dr. N. R. Dhar, and wishes to record here his sincere thanks.

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Condensation of Amidines with Ethoxy-methylene Derivatives of β -Ketonic Esters, β -Diketones and Cyanacetic Ester.

Part II.

By

PROFULLA CHANDRA MITTER

AND

NIRMALANANDA PALIT.

It has been shown by one of us that benzamidine and *p*-toluamidine condense readily with ethylethoxymethylene acetoacetate and ethylethoxymethylene malonate giving rise to pyrimidine derivatives (Mitter and Bardhan, J. Chem. Soc., 1923, 123, 2179). This work has now been extended, on the one hand by using aliphatic amidines like acetamidine and guanidine and on the other hand by taking more complex amidines like anisamidine and naphthamidine. With the exception of acetamidine which apparently decomposes in course of the reaction, the expected pyrimidines have been obtained in every case.

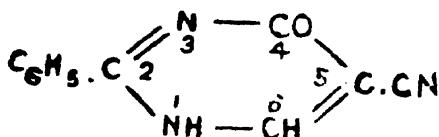
We have also studied the condensation of amidines with ethylethoxymethylene cyanacetate as it was expected that the presence of the additional reactive centre—the cyanogen group—will make its presence felt by giving rise to other sets of condensation products. Our expectations in this respect have been fully realised and we have in the majority of the cases investigated, got

at least one product—in some cases even two—in addition to the expected cyano-pyrimidine. The constitution of these substances is still under investigation and will form the subject-matter of a later communication.

EXPERIMENTAL

(a) Pyrimidines from Ethyl Ethoxymethylenecyanacetate.

Condensation with Benzamidine: Formation of 4-Keto-5-cyano-2-phenyl-1:4-dihdropyrimidine.



The reaction was brought about by treating benzamidine hydrochloride (2·4 gms.) suspended in slightly more than the calculated amount of sodium ethoxide solution, with ethyl ethoxymethylenecyanacetate (2·2 gms.) and digesting the mixture for about an hour. The alcohol was then removed by evaporation, the residue dissolved in water and the liquid acidified with dilute hydrochloric acid. The condensation product separated as a thick white deposit which when dry weighed 3 gms. Glacial acetic acid was found to be the only solvent that dissolved it completely and from this solution a very poor yield of fine glistening needles were obtained melting at 295° C.

(Found: N = 21.52. C₁₁H₇ON₃ requires N = 21.3 per cent.)

From the mother-liquor was obtained two substances, one melting between 145° - 52° and the other at 130° , the constitutions of which have not yet been definitely ascertained.

The hydrolysis of the cyano-compound described above was effected by treating it with an excess of sulphuric

acid diluted with molecular proportion of water (*i.e.*, with $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$). The substance dissolved in the acid freely in the cold. The solution was boiled under reflux for an hour. On cooling and diluting with water the product separated which crystallized from dil. acetic acid in short elongated rectangles melting with effervescence to a clear liquid at 271°C .

(Found : N = 12·68. $\text{C}_{11}\text{H}_8\text{O}_3\text{N}_2$ requires N = 12·96 per cent.)

Condensation with p-Toluamidine: Formation of 4-Keto-5-cyano-2-tolyl-1:4-dihdropyrimidine.

The condensation product separated from glacial acetic acid in white flaky plate-like crystals. It melts at $303\text{--}4^\circ\text{C}$ to a clear colourless liquid and like other cyanopyrimidines, it is insoluble in all other common organic solvents. (Found : N = 20·08. $\text{C}_{12}\text{H}_9\text{ON}_3$ requires N = 19·9 per cent.) Besides the above, another impure product was obtained from the mother-liquor.

The hydrolysis product crystallized from dilute acetic acid in prismatic needles melting at 282°C . The substance was found to be identical with the compound obtained by hydrolysing the ester from toluamidine and ethyl-ethoxymethylenemalonate. (Mitter and Bardhan J. Chem. Soc., 123, 2179).

Condensation with p-Anisamidine: Formation of 4-Keto-5-cyano-2-anisyl-1:4-dihdropyrimidine.

The substance was obtained from glacial acetic acid as a greenish, white crystalline powder melting at 286°C .

(Found : N = 18·54. $\text{C}_{12}\text{H}_9\text{O}_2\text{N}_3$ requires N = 18·50 per cent.)

The carboxylic acid was obtained by hydrolysis of the above in the form of meshes of very fine needles and

crystallized from a large excess boiling alcohol in stars of concentric needles, which melted at 271°C. with effervescence. The substance is sparingly soluble in the common solvents. The same acid has been obtained by hydrolysing the ester formed from anisamidine and ethyl ethoxymethylenemalonate.

(Found : N = 11·59. C₁₂H₁₀O₄N₂ requires N = 11·38 per cent.)

Condensation of β-Naphthamidine : Formation of 4-Keto-5-cyano-2-β-naphthyl-1 : 4-dihydropyrimidine.

The yellow condensation product was crystallized from glacial acetic acid with the addition of animal charcoal. On cooling long slender hair-like yellow needles were obtained which melted sharply to an yellow liquid at 305°-6°C.

(Found : N = 16·83. C₁₅H₉ON₃ requires N = 17·0 per cent.)

The hydrolysis product of the above is scarcely soluble in any of the common organic solvents. It dissolves in a very large excess of glacial acetic acid. Hence it was purified only by repeated precipitation from alkali solution by dilute hydrochloric acid. It melts with effervescence at 291°C.

(Found : N = 10·65. C₁₅H₁₀O₃N₂ requires N = 10·52 per cent.)

From the mother-liquor was obtained a substance melting at 147°-148° which is still under investigation.

(b). Pyrimidines from Ethyl Ethoxymethyleneacetooacetate.

Condensation with Guanidine : Formation of Ethyl-4-methyl-2-aminopyrimidine-5-carboxylate.

Sodium (0·35 gms.) was dissolved in alcohol and the solution well-cooled by immersion in ice water.

Guanidine carbonate (2·2 gms.) was then added when the free amidine was liberated. To this was introduced the ethyl ethoxymethyleneacetoacetate slowly drop by drop with constant stirring. The whole mass solidified almost instantaneously and the last drops of the ethoxymethylene compound gave a rose red coloration. After standing in ice for more than a quarter of an hour more alcohol was added, and half of the mixture taken in a separate flask and gently boiled over water-bath for an hour, while the other half was left undisturbed in the cooling bath. The two products, obtained under these two different conditions were however found to be the same. These were filtered, washed well with water and crystallized from alcohol in short thin needles thickly interwoven into a mesh. It could also be very easily crystallized from acetone. It melted at 222°C.

(Found : N=23·6. C₁₁H₁₁O₂N₃ requires N=23·2 per cent.)

The hydrolysis of the ester was effected by heating it with alcoholic potassium hydroxide under reflux. The alcohol was then evaporated off, the residue dissolved in water, filtered and just acidified with dilute hydrochloric acid, excess being avoided since the amido acid is soluble in mineral acids. The precipitate was washed with water and purified by repeated precipitation from its solution in alkali by dilute mineral acid. The substance melts at 256-8°C with decomposition.

(Found : N=27·79. C₆H₇O₂N₃ requires N=27·45 per cent.)

Condensation with Anisamidine: Formation of Ethyl 2-anisyl-4-methylpyrimidine-5-carboxylate.

The action of anisamidine on ethylethoxymethylene-acetoacetate takes place readily when solutions of sodium

(1 atom) and the hydrochloride of the base (1 mol.) in alcohol are mixed, the ethoxymethylene derivative (1 mol.) cautiously added and the mixture heated on the water-bath in the usual manner. No deep coloration or setting to a solid could be observed. On cooling a part only separated. The liquid was allowed to stand after the addition of a little water, when clusters of crystalline needles were obtained. The substance was very soluble in alcohol. It melted to a clear liquid at 80°C.

(Found : N = 10.8. $C_{15}H_{16}O_3N_2$ requires N = 10.3 per cent.)

The corresponding acid was obtained without much difficulty when the ester was boiled with alcoholic potash for four hours under reflux. The acid crystallized from methyl alcohol in short silky needles melting at 232-3°C.

(Found : N = 11.6. $C_{13}H_{12}O_3N_2$ requires N = 10.9 per cent.)

Condensation with Naphthamidine : Formation of Ethyl-2-β-naphthyl-4-methylpyrimidine-5-carboxylate.

This consideration takes place with the utmost ease when the usual procedure is adopted. On the addition of ethyl ethoxymethyleneacetate to the liberated amidine, the whole set to a solid mass. The mixture was then boiled for 40 minutes. On cooling clusters of concentric needles were obtained, which could be very easily crystallized from alcohol. The substance melts at 118°C.

(Found : N = 9.77. $C_{18}H_{16}O_2N_2$ requires N = 9.58 per cent.)

The ester was hydrolysed as usual by digestion with alcoholic potash for four hours, the potassium salt being obtained by distilling off the alcohol. It was dissolved in water, filtered from the suspended impurities and acidified by dilute mineral acid when a voluminous

gelatinous ppt. was obtained which crystallized from alcohol and melted at 245-46°C.

(Found : N=10·8. C₁₆H₁₂O₃N₂ requires N=10·6 per cent.)

(c) Pyrimidines from Ethoxymethyleneacetylacetone.

Condensation with Anisamidine : Formation of 5-Acetyl-2-anisyl-4-methylpyrimidine.

A mixture of the amidine hydrochloride and ethoxymethylene compound in sodium ethoxide solution was gently boiled for an hour. The deep orange colour which developed at first gradually faded and the condensation product separated on cooling in crystals that were filtered, washed and repeatedly crystallised from dilute acetone with water, with the aid of animal charcoal. Even after three such purifications the substance melted slowly between 113°-15°C and it could not be further purified.

(Found : N=11·63. C₁₁H₁₁O₂N₂ requires N=11·57 per cent.)

Condensation with Naphthamidine : Formation of 5-Acetyl-2-β-naphthyl-4-methylpyrimidine.

The reaction was exactly analogous to that described above the condensation being completed by boiling for an hour. A very poor yield of the product was obtained. On crystallisation from acetone solution with addition of animal charcoal it melted at 151-53°C.

(Found : N=10·88. C₁₇H₁₄O₄N₂ requires N=10·70 per cent.)

(d) Pyrimidine from Ethyl Ethoxymethylenemalonate.

Condensation with Guanidine : Formation of Ethyl 4-keto-2-amido-1 : 4-dihydropyrimidine-5-carboxylate.

The guanidine carbonate was added to the alcoholic solution of sodium ethoxide, quickly followed by the

ethyl ethoxy-methylene-malonate and the mixture was constantly stirred. A solid began to separate and within a little over a quarter of an hour the whole set to a hard mass. Instead of heating on the water-bath, it was left undisturbed overnight when it was observed that the hard mass slackened to a loose white deposit. The alcohol was evaporated. The aqueous solution of the residue was just acidified and the precipitate filtered and washed. It hardly dissolved in the neutral solvents. Although fairly soluble in glacial acetic acid, it could not be obtained in any well defined crystalline form but in minute grains melting at 285°C.

(Found : N = 23·14. $C_7H_9O_3N_3$ requires N = 22·95 per cent.)

The corresponding acid from the ethyl ester was obtained by hydrolysing the latter with alcoholic potash for five hours. The alcohol was evaporated, residue dissolved in water, filtered and made just acid with dilute mineral acid when white granular crystals were obtained. It did not dissolve in alcohol, acetone, benzene, chloroform, etc., and so it was purified by precipitation from alkaline solution. It melted with decomposition at 238°C.

(Found : N = 27·02. $C_5H_5O_3N_3$ requires N = 27·09 per cent.)

Isolation of the Intermediate Product in the Condensation of Guanidine with Ethyl Ethoxymethylenemalonate.

Formation of $NH_2C(NH_2) : N.COO.C(COOEt) : CHOEt$. Ethyl ester of Ethoxy-methylene malon-guanidic acid.

To investigate what the solid first separates in the above condensation, the mixture was not allowed to stand overnight but the process of condensation interrupted, by filtering it after an hour, washing the ppt. with alcohol and decomposing the sodium compound with glacial

acetic acid. Dilute hydrochloric acid could not be used here since the whole dissolved in it owing no doubt to the pronounced basic nature of the liberated product. When crystallized from glacial acetic acid it was obtained in grains that melted at 295°C. with a shrinking far below this temperature. The combustion value agrees with the supposition that guanidine and ethoxymethylene compound have combined in it to an open chain derivative with the elimination of only one molecule of alcohol.

(Found : N = 18.73. C₉H₁₅O₄N₃ requires N = 18.33.)

Transformation of the Intermediate Compound to (NH₂)₂C : N.COCH₂ COOH, Malon-guanidic acid.

The hydrolysis of the ethyl ester and removal of the hydroxymethylene group was effected by dissolving it in 50% hydrochloric acid and heating under reflux. Immediately on boiling a granular product separated and within five minutes the quantity was considerable. After continuing the hydrolysis for an hour, it was filtered and washed. It melts at 254°C with decomposition.

(Found : N = 28.68. C₄H₇O₃N₃ requires N = 28.96 per cent.)

Condensation with Anisamide. Formation of Ethyl 4-keto-2-anisyl-1 : 4-dihydropyrimidine-5-carboxylate.

The mixture of ethyl ethoxymethylenemalonate, anisamide and sodium dissolved in alcohol was boiled on the water-bath for an hour, the alcohol evaporated and the aqueous solution acidified as usual. The condensation product was collected, washed and crystallized from a large excess of boiling alcohol. It melts at 222°-24°C.

(Found : N = 10.35. C₁₄H₁₁O₄N₂ requires N = 10.20 per cent.)

The hydrolysis of the above ethyl ester gave an acid which was found to be the same as was obtained by hydrolysing the cyanopyrimidone produced by condensing guanidine with ethyl ethoxymethylenecyanacetate.

Condensation with β -Naphthamidine: Formation of Ethyl-4-keto-2-naphthyl-1 : 4-dihdropyrimidine-5-carboxylate.

The reaction was brought about exactly according to the above procedure. The product was repeatedly crystallised from glacial acetic acid and yet the slight greenish-yellow tinge and its shrinking below the melting point could not be got rid of. It melted at 213-15°C.

The corresponding acid, obtained by digesting the above product with alcoholic potash for 5 hours, was found identical with the one derived from the cyano compound by boiling the latter with sulphuric acid.

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Received, March 12, 1925.

Dyes derived from Oxalyldibenzylketone..

Part I.

Azine and Azonium Derivatives.

By

GOPĀL CHANDRA CHAKRAVARTI.

Dibenzylketone condenses with oxalic ester in presence of sodium ethoxide (Claisen and Ewan, Annalen, 1885, 284, 250) yielding oxalyldibenzylketone which may be otherwise called 2 : 4 : 5-triketo-1 : 3-diphenyl-R-pentamethylene. This substance is an α -diketone and may be expected to condense with *o*-diamines to form azines. Claisen and Ewan (*loc. cit.*) condensed it with *o*-tolylenediamine. The present author has condensed it also with *o*-phenylenediamine, 1 : 2-naphthylene diamine and brom- and chlor-tolylenediamines in order to compare the colour of these azines with that of the phenanthrazines and acenaphthazines.

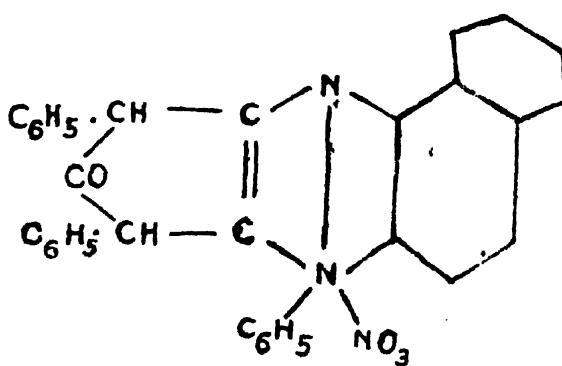
It has been found that the products nearly resemble the phenanthrazines and acenaphthazines in colour and dyeing properties.

It will be observed that both phenanthraquinone and acenaphthaquinone contain three nuclei which are fused together. But in oxalyldibenzylketone two phenyl residues are only linked with a pentamethylene ring. As the presence of condensed ring systems acts "bathochromically," that is, tends to increase the intensity of colour in compounds, it might be reasonably supposed that phenanthraphenazine and acenaphthaphenazine would be more strongly coloured than the azine from oxalyldibenzylketone. But since that is not the case, it is evident that the presence of the additional

chromophore, viz., the CO group in the molecule greatly intensifies the colour in the latter type of compounds. Most of the azines described above are bright yellow substances which show characteristic colour reactions with concentrated sulphuric acid and dye unmordanted wool in uniform and fine shades from a neutral bath.

It was supposed that the dying properties of these dyestuffs would be greatly augmented if these compounds could be made soluble in water. With this object in view oxalyldibenzylketone was condensed with *o*-phenylenediamine sulphonic acid, 1 : 2-naphthylenediamine sulphonic acid and diaminonaphthol sulphonic acids. But the products so obtained, although somewhat soluble in water, were found to possess no superior dyeing properties.

It has been observed that in the azine series the tinctorial properties of a compound are greatly enhanced by the conversion of a nitrogen atom from the tervalent to the quinquevalent state, that is, by changing an *azine* to an *azonium* compound. With this object in view oxalyldibenzylketone was condensed with 1-amino-2-phenylamino-naphthalene in the presence of hydrochloric and nitric acids. The chloride so obtained has a brown colour while the nitrate is scarlet red. But contrary to expectation these compounds have not very marked dyeing properties. The nitrate may be represented by the following diagram :



A further study of the azonium compounds as well as the glyoxalines derived from oxalyldibenzylketone is in progress.

EXPERIMENTAL.

Product from orthoPhenylenediamine and Oxalyldibenzylketone.—2·6 gms. of oxalyldibenzylketone are mixed with 1·1 gm. of *o*-phenylenediamine and 50 c. c. of absolute alcohol. The mixture is boiled under reflux for 3 to 4 hours. The precipitate obtained on cooling is crystallised from acetone. It is a bright pink crystalline substance melting at 251°. It dissolves in concentrated sulphuric acid with a deep pink colour which turns brown on dilution. The freshly-precipitated substance dyes yellow shades on unmordanted wool from neutral bath.

(Found : C = 82·31; H = 4·65; N = 7·80. $C_{23}H_{16}N_2O$ requires C = 82·14; H = 4·76 and N = 8·33 per cent.)

Product from 1 : 3 : 4-orthoTolylenediamine and Oxalyldibenzylketone.—The precipitate obtained by boiling an absolute alcoholic solution of 5·2 gms. of oxalyldibenzylketone and 2·5 gms. of *o*-tolylenediamine for 4-5 hours is crystallised from a yellow mixture of pyridine and water. The prismatic crystals melt at 285° and dissolve in concentrated sulphuric acid with a pink solution. The compound dyes brown shades on wool.

(Found : N = 7·89. $C_{24}H_{18}N_2O$ requires N = 8·00 per cent.). (Cf. Claisen and Ewan, *loc. cit.*)

Product from 1 : 3 : 4 : 5-Bromtolylenediamine and Oxalyldibenzylketone.—The compound is obtained similarly by heating equimolecular quantities of the diamine and the ketone in alcoholic solution and crystallising it from a mixture of pyridine and water. The crystals are

ochre-coloured prisms melting above 300° . They dissolve in concentrated sulphuric acid with a deep red colour and dye wool in pink shades.

(Found : Br = 18.10. $C_{24}H_{17}BrN_2O$ requires Br = 18.41 per cent.).

Product from 1 : 2-Naphthylenediamine and Oxalyldibenzylketone.—It is obtained as the previous compound and crystallised from xylene. The crystals are deep yellow prisms melting at 288° and dissolving in conc. sulphuric acid with a violet solution. They dye wool in gamboge shades.

(Found : N = 7.51. $C_{27}H_{19}N_2O$ requires N = 7.25 per cent.).

Product from 1 : 2 : 3-orthoPhenylenediamine sulphonic Acid and Oxalyldibenzylketone.—Equimolecular quantities of the ketone and the sulphonic acid are boiled with a little water for 5-6 hours. The precipitate is extracted with a large quantity of water which on cooling deposits yellow crystals of the azinesulphonic acid.

(Found : N = 6.54. $C_{23}H_{16}N_2O_4S$ requires N = 6.73 per cent.).

Product from 1 : 2-Diamino-8-naphthol-6-sulphonic Acid and Oxalyldibenzylketone.—The product is obtained in the same way as the previous one and the precipitate purified through the calcium salt. It is sparingly soluble in hot water.

(Found : N = 5.75. $C_{27}H_{12}N_2O_5S$ requires N = 5.81 per cent.).

Product from 1 : 2 : 4-Naphthylenediamine Sulphonic Acid and Oxalyldibenzylketone.—Equivalent quantities

of the sulphonic acid and the ketone are boiled with a small quantity of water and the product purified through the calcium compound as above. It is obtained as a yellow amorphous precipitate.

(Found : N = 5.93. C₂₇H₁₈N₂O₄S requires N = 6.01 per cent.)

Product from 1 : 6 : 3 : 4-Chlortolylenediamine and Oxalyldibenzylketone—2.5 gms. of oxalyldibenzylketone and 1.3 gms. of the diamine are boiled in absolute alcoholic solution for 5-6 hours. The crystalline precipitate is recrystallised from a mixture of pyridine and water and melts above 300°.

(Found : N = 7.14. C₅₄H₁₇ClN₂O requires N = 7.28 per cent.)

Product from 1-Amino-2-phenylamino-naphthalene and Oxalyldibenzylketone.—The amine and the ketone are dissolved in equimolecular quantities in glacial acetic acid and a few c.c.s of conc. hydrochloric acid are added to the mixture and warmed. A precipitate of the hydrochloride is at once formed, and is crystallised from alcohol in brown crystals, m. p. 195°.

(Found : N = 5.62. C₈H₂₃N₂OCl requires N = 5.75 per cent.)

The nitrate is obtained like the chloride by using concentrated nitric acid in the above reaction instead of hydrochloric acid. The dark red solution on treatment with one or two drops of water gives a scarlet red crystalline precipitate of the nitrate which is washed with alcohol and ether. This is recrystallised from absolute alcohol and melts above 300°. It gives a dark brown

solution in conc. sulphuric acid and dyes unmordanted wool in light brown shades.

(Found : N=8·23. $C_{32}H_2N_3O_4$ requires N=8·18 per cent.).

In conclusion my thanks are due to my friend Mr. S. B. Dutt for helping me with some chemicals. My best thanks are also due to Sir P. C. Ray for his kind encouragement throughout this investigation.

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Received May 8, 1925.

Reduction of Symmetrical Dichloracetone by Yeast.

BY

HEMENDRA KUMAR SEN

AND

CHITABANJAN BARAT.

It was found by one of us (*J. Indian Chem. Soc.*, 1924, 1, 1) that unsymmetrical dichloracetone lends itself to easy reduction by yeast, whereas monochloracetone gave very indifferent results, acting poisonously towards yeast even in weak concentrations. It was, therefore, considered desirable to extend this yeast reduction process to some other chlorinated ketones,¹ as the inhibiting influence of these upon yeast would probably furnish at least a qualitative measure of their physiological activity. Attempts are being made to regulate the addition of chlorinated ketones to the fermenting sugar solution with the help of an electric potential recorder first described by Potter (*Proc. Royal Society*, 1911, B, 84, 260), so that the influence of inhibition due to concentration may be as near as possible measured or eliminated and useful light thrown on the mechanism of the

¹ We notice that the biochemical reduction of chlorinated ketones, although for the first time introduced by one of us, has been undertaken by another worker (Pietro Santomauro, *Biochem. Zeit.*, 1924, 151, 48) without even the customary references, to which we draw the attention of colleagues.

3-carbon theory of alcoholic fermentation. Besides, the use of chlorinated secondary alcohols or their urethane derivatives as hypnotics suggested by one of us (*loc. cit.*), gives additional interest to biochemical reduction processes of the said nature. The experiments further point to the important function which the enzyme 'reductase' plays in general alcoholic fermentation, and from which a connected chemical representation of the process of alcoholic fermentation has been attempted.*

EXPERIMENTAL.

Symmetrical dichloracetone $\text{CH}_2\text{Cl}.\text{CO}.\text{CH}_2\text{Cl}$ was prepared by the oxidation of dichlorhydrin (symmetrical dichlorisopropyl alcohol). The obtaining of pure dichlorhydrin in any quantity, which is an industrial product of some importance, was rather difficult, and the yield stated to have been obtained by Carius (*Annalen*, 168, 43) could in no case be attained, a little more than half of the recorded yield being available. Using 150 grams pure glycerine and 375 grams of Merck's sulphur chloride (freshly distilled before use), only 62 grams of dichlorhydrin was obtained which collected mostly at 178°C and corresponded to 42% of the theory. The purity of the alcohol was established by preparing the known urethane derivative which melted at 80-81° C.

The method of preparing symmetrical dichloracetone which is described in *Annalen* (208, 353) giving a very poor yield, was modified as follows :—

25 grams of dichlorhydrin was taken in a 250 c.c. stoppered bottle and 20 grams of finely powdered (120 mesh) potassium dichromate were added to it and mixed well. 30 grams of concentrated sulphuric acid diluted with 30 c.c. of water and cooled, were then added

* The paper was read before the Chemical Section of the Indian Science Congress, at its sitting in Benares (1925).

to the mixture little by little during about $2\frac{1}{2}$ hours, the bottle being kept cool in ice and shaken from time to time. In the addition of the acid, care was taken that no evolution of gas took place, as this leads to further oxidation of the ketone. It was observed that the reduction of the dichromate took place very slowly in the cold, as shown by the colour of the mixture, which was, therefore, allowed to stand after addition of the total quantity of acid, at room temperature (25°C) for a quarter of an hour, and shaken repeatedly. The oxidation proceeded and the solution showed a tendency to warm up and liberate gas. The bottle was then quickly replaced in ice water and the reaction mitigated. The oxidation was brought to completion in this way, and the mixture finally slightly warmed up on the water-bath. It was cooled, extracted with ether, the ethereal solution well shaken up with a freshly prepared strong solution of sodium bisulphite when all the ketone went into the aqueous layer, leaving the unconverted dichlorhydrin dissolved in the ethereal layer. The aqueous layer was separated, decomposed with dilute sulphuric acid and distilled, the ketone, being volatile in steam, distilled over with the aqueous distillate, which was extracted with ether. The ethereal solution was dried with anhydrous sodium sulphate, the ether evaporated and the residual oil fractionated. An oily liquid distilling at 172°C was collected, which mostly solidified into a beautiful crystalline mass in the condenser, and was symmetrical dichloracetone. The crystals melting at 45°C have a pungent and tear-bringing odour. The yield amounted to 6 grams.

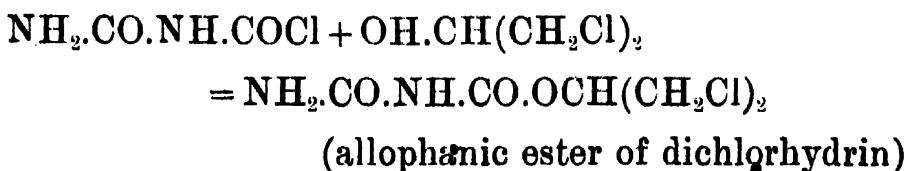
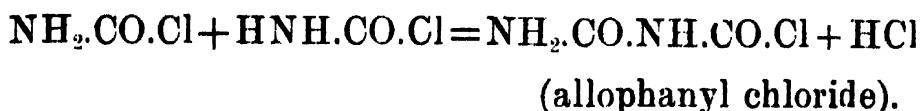
The reduction of symmetrical dichloracetone was conducted in the same way as in the case of unsymmetrical dichloracetone described before (*loc. cit.*). 250 grams of cane sugar dissolved in 2·5 litres of tap

water to which sufficient fresh yeast was added, were slowly treated with a 25% alcoholic solution of symmetrical dichloracetone, soon after brisk fermentation had commenced. Nine grams of the chloroketone were added in 4 hours, and the mixture allowed to ferment overnight. Next day in order to ensure complete fermentation of sugar, 100 grams of pressed yeast were further added, and the mixture allowed to stand for two days with occasional shaking. The clear liquid was next decanted and distilled under reduced pressure. The residue after decantation was washed two or three times with water and the aqueous extract distilled under reduced pressure as usual. The total distillate which amounted to about 2·8 litres was extracted with two pounds of ether, the ethereal solution dried over ignited sodium sulphate, and the ether expelled on the water-bath. Five c.c. of an oily liquid remained behind, which when fractionated gave 4·8 grams of a clear liquid boiling at 178°C, and identical with dichlorhydrin.

The urethane derivative, already known (Otto, *J. pr. Chem.*, [2], 44, 20) and patented under the name, aleudrin (Mass, *Biochem. Zeit.*, 143, 65) was prepared as follows :—

Equimolecular proportions of chloroformamide and symmetrical dichloracetone were dissolved separately in dry ether and the two mixed in the cold. The mixture was allowed to stand at the room temperature for fifteen minutes, and then heated on the water-bath to expel all the ether. The residue was treated with water to decompose any remaining chloroformamide and to dissolve out the solid ammonium chloride. The oily mass on scratching soon set into a white crystalline solid which when recrystallised from alcohol, melted at 80-81°C. A mixture of this with the urethane compound from the original dichlorhydrin also melted at 80-81°C.

If, however, an excess of chloroformamide (two molecular proportion to one of dichlorhydrin) be employed, the allophanic ester is produced :—



This compound melts at 182°C. The crude product, however, seemed to be never free from the urethane derivative, as after crystallising the allophanic ester from hot 60% alcohol, the mother-liquor when cooled with ice gave a fresh crop of crystals which did not melt sharply.

Found : N = 13·14 ; Cl = 32·56. $\text{C}_5\text{H}_8\text{O}_3\text{N}_2\text{Cl}_c$ requires N = 13·02 and Cl = 33·02 per cent.

We take this opportunity of expressing our gratitude to Dr. K. C. Bose of Dr. Bose's Laboratory, Ltd., for supplying the yeast required for our experiments, and placing the resources of his distillery at our disposal.

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Received, May 22, 1925.

Ortho-Amido-phenylhydrazine and some Interesting Heterocyclic Compounds derived from it.

BY •

PRAPHULLA CHANDRA GUHA

AND

SUDHANYA KUMAR RAY.

Although *m*-amido- and *p*-amido-phenylhydrazines and a good number of compounds derived from them are known (Bischler and Brodsky, *Ber.*, 22, 2810; Griess, *Ber.*, 18, 963; Freund, *Ber.*, 16, 1320), no systematic investigation has been carried out with *o*-amido-phenylhydrazine, it being itself unknown. Bischler (*Ber.*, 22, 240) describes a method for the preparation of *o*-amido-phenylhydrazine, but there is no mention of its melting point, method of separation and purification, nor does he give any analytical results of his compound. The natural conclusion to be drawn from the work of Bischler is that he merely got some indication of the formation of this compound, but he could not actually isolate it.

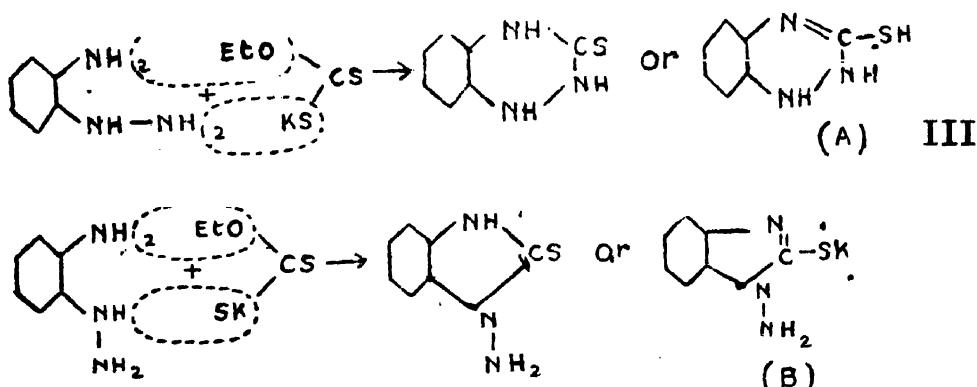
Reference should be made here to the works of Hempell (*J. pr. Chem.*, 41, 170) and of Nietzki (*Ber.*, 22, 3221). The former prepared the methyl derivative of *o*-amido-phenylhydrazine from *o*-nitro-methylaniline by the action of nitrous acid and then reducing the nitroso derivative so formed, whilst Nietzki prepared *o*-amido-phenylhydrazine sulphonic acid from *o*-nitraniline sulphonic acid in the usual manner. Franzen (*Ber.*, 40,

909) obtained the benzal derivative of *o*-amido-phenylhydrazine by reducing the benzal compound of *o*-nitrophenylhydrazine with sodium bisulphite and effected the ring closure of his amido-hydrazine derivative by two per cent. hydrochloric acid and steam.

o-Amido-phenylhydrazine has now been prepared by reducing *o*-nitro-phenylhydrazine with stannous chloride and hydrochloric acid. The success of the method depends on the concentration of the hydrochloride solution in the absence of air and precipitating it with ether from an alcoholic solution.

Both the amino and hydrazino groups react with phenyl mustard oil forming 1-phenylthiocarbamido-phenyl 4-phenyl-thiosemicarbazide PhNH.CS.NH.C₆H₄.NH.NH.CS.NHPh (I). An analogous compound has also been obtained from *o*-tolyl mustard oil. Benzaldehyde gives a dibenzylidene derivative PhCH:N.C₆H₄.NHN:CHPh (II).

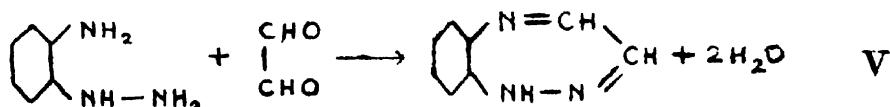
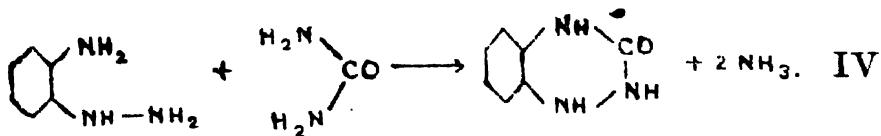
With potassium ethylxanthate it gives a compound of the empirical formula C₇H₇N₃S which may represent either the benzotriazine compound (A) or the benzodiazole compound (B) as shown below :



Both of these formulae contain a thiol or mercaptanic group. A compound of the formula (B) should readily

form a hydrochloride and react with benzaldehyde to form a benzal derivative, whereas a compound of the formula (A) should be acidic in nature and should not form a hydrochloride or a benzal derivative (Compare Guha and De, *J. Chem. Soc.*, 1924, 125, 1215; Arndt and Bielich, *Ber.*, 56, 809). The compound $C_7H_7N_3S$ is found to be acidic in nature and to form alkali salts, a yellow mercaptide with mercuric chloride, a disulphide and a benzoyl derivative showing the presence of a mercaptanic group, and being in agreement with the benzothiazine formula (A) for the compound.

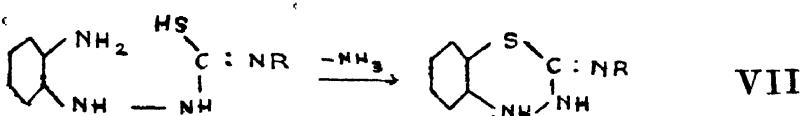
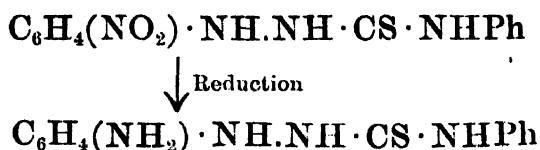
Urea condenses with amido-phenylhydrazine to form benzo-keto-tetrahydrotriazine (IV), while glyoxal sodium bisulphite reacts to form a benzo-hepta-triazine compound (V), thus:



the latter being basic, combines with one molecule of sulphurous acid (Compare Cain, *J. Chem. Soc.*, 1914, 105, 1441).

o-Nitrophenylhydrazine (*Ber.*, 22, 2801) reacts with thiocarbamides in the normal way giving *o*-nitrophenyl-thiosemicarbazides. When these thiosemicarbazides are reduced with tin and hydrochloric acid, the reaction proceeds in two distinct stages. First, the nitro group is reduced to the corresponding amino derivative (VI), which again in presence of hydrochloric acid

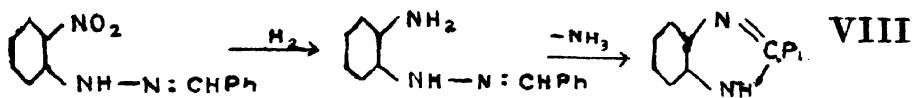
loses a molecule of ammonia to yield a benzo-thiodiazine derivative, thus :



The same benzo-thiodiazine compound (m. p. 151°) was also obtained when the amino compound (m. p. 253°) was treated with acetic anhydride.

The thiodiazine constitution given above follows from the fact that it is insoluble in alkali and does not give any mercaptide or thioether or disulphide.

The benzal derivative of *o*-nitro-phenylhydrazine yields on reduction with tin and hydrochloric acid, phenylbenziminazole hydrochloride from which the base can be liberated by ammonia, thus :—



μ -Phenylbenziminazole

EXPERIMENTAL.

Preparation of o-Amido-phenylhydrazine hydrochloride.

A mixture of 10 gms. of *o*-nitrophenylhydrazine hydrochloride, 45 gms. of stannous chloride, 60 c.c. of concentrated hydrochloric acid and a little water was taken in

a stoppered bottle and shaken vigorously for 2-3 hours in a shaking machine, when the reduction was complete. The mixture became hot and dark in colour. The contents were then diluted with 600-700 c.c. of water, warmed and tin removed by hydrogen sulphide. The largely diluted solution acquired a brownish red colour on exposure to air, and the concentration was therefore carried out under vacuum in the absence of air as far as practicable.

The fairly concentrated solution on cooling gave crystals which were slightly brownish in colour. It was purified by precipitating by ether from an alcoholic solution as a white powder and was dried in a vacuum desiccator. M. p. 263-265° with decomposition. Yield 3-4 gms.

(Found : N = 21.18. C₆H₉N₃, 2HCl requires N = 21.42 per cent.).

The Free Base : o-Amido-phenylhydrazine.—The free base was obtained by adding ammonia or sodium acetate to the hot concentrated aqueous solution of the hydrochloride, as a reddish brown amorphous mass. It was filtered and crystallised from dilute alcohol avoiding the presence of air as much as possible, in contact with which it soon gets coloured brownish black. It dissolved in acids and melted between 295-302° with decomposition showing it to be rather impure.

o-Amido-phenylhydrazine and Phenyl Mustard Oil : Formation of 4-Phenyl-1-ortho-phenyl-thiocarbamido-phenyl-thiosemicarbazide, C₆H₄(NH.CS.NHPh).NH.NH.CS.NHPh (I).

An alcoholic solution of 2 gms. of *o*-amido-phenylhydrazine hydrochloride (1 mol.) and 1.4 gms. of phenyl

mustard oil (1 mol.) was heated on a water-bath under reflux for 2-3 hours. The reaction product was then poured into water, when a white solid separated out. This was crystallised from dilute alcohol in shining white rectangular plates, which melted at 80° and was soluble in hot water and in cold concentrated alkali. Yield 1.1 gm.

(Found: S=16.02. C₂₀H₁₈N₅S₂ requires S=16.29 per cent.)

o-Amido-phenylhydrazine and o-Tolyl Mustard Oil : Formation of 4-Tolyl-1-tolyl-thiocarbamido-phenyl-thiosemicarbazide.

The method of preparation was the same as in the case of the preceding compound. Yield 0.7 gm. from 0.5 gm. of *o*-amido-phenylhydrazine hydrochloride and 0.4 gm. of *o*-tolyl mustard oil. M. p. 282°C.

(Found: S=15.8. C₂₂H₂₃N₅S₂ requires S=15.2 per cent.)

Dibenzylidene Derivative of o-Amidophenyl-hydrazine (II).

A dilute alcoholic solution of 0.8 gm. of *o*-amido-phenylhydrazine hydrochloride and 0.6 gm. of benzaldehyde was heated on a water-bath under reflux for about 2 hours. Some alcohol was then distilled off and on adding water to the residue a white solid separated out. Any unconverted benzaldehyde was removed by passing steam through the solution. On concentration and cooling a white substance came down; this was dissolved in the minimum quantity of hot water and obtained as a white amorphous powder on scratching the sides of the vessel.

M. p. 206-207°. It was the hydrochloride of a base and gave silver chloride with silver nitrate solution. (Found : N=10.95. C₂₀H₁₇N₃.HCl.2H₂O requires N=11.30 per cent.). The free base was liberated from it as a white flocculent precipitate by boiling with ammonia.

o-Amido-phenylhydrazine and Potassium ethylxanthate: Formation of 2-Thio-1:2:3:4-tetrahydro-5:6-benzo-1:3:4-triazine (III).

A mixture of 1.2 gm. of *o*-amido-phenylhydrazine hydrochloride, 3 c.c. of alcoholic potash (1 c.c.=.12 gm. of KOH) and one gram of carbon bisulphide in alcoholic solution was heated on a water-bath for 6-7 hours under reflux. The reaction product was poured into water when a yellow precipitate came down, which was filtered off, washed with cold water and crystallised from hot water containing a few drops of hydrochloric acid. M.p. 298-300°. It was soluble in alcohol and in cold dilute alkali giving a deep yellowish brown solution and gave a beautiful blood-red colour with potassium ferricyanide.

(Found : N=24.95 ; S=19.81. C₇H₇N₃S requires N=25.45 ; S=19.39 per cent.)

The *Benzoyl* derivative.—0.5 gm. of the benzo-triazine compound when benzoylated by Schotten-Baumann process gave about 0.3 gm. of a light yellow compound which when crystallised from alcohol melted at 174°.

The *disulphide* was prepared by adding iodine solution to an alcoholic solution of the benzo-triazine compound and then adding an excess of water when it was

completely precipitated as a yellow amorphous powder. It was washed with dilute potassium iodide, water and finally with alcohol and was found to be insoluble in all ordinary solvents. M.p. 208-210°.

Urea and o-Amido-phenylhydrazine hydrochloride : Formation of Benzo-keto-tetrahydrotriazine (IV).

One gm. of *o*-amido-phenylhydrazine hydrochloride was intimately mixed with 0·6 gm. of urea in a dry clean mortar and the mixed powder was then heated in a dry boiling tube on an oil-bath to 135-145°C for about $2\frac{1}{2}$ hours with occasional stirring. Ammonia evolved profusely and the contents became first semi-solid and after a while formed into a solid cake, when the evolution of ammonia ceased. The cake was carefully detached from the boiling tube, powdered and triturated with water, when a yellowish white powder was obtained which was crystallised from hot water (slightly acidulated with hydrochloric acid) in long rectangular plates. It melted at 310-312° and sublimed slowly at a higher temperature into mica-like plates. The substance was insoluble in acid but soluble in cold alkali.

(Found : N = 22·21. C₇H₇ON₃·2H₂O requires N = 22·58 per cent.)

o-Amido-phenylhydrazine and Glyoxal : Formation of a Benzo-hepta-triazine Compound (V).

An aqueous solution of 1 gm. of *o*-amido-phenylhydrazine hydrochloride and 1·5 gm. of glyoxal sodium bisulphite was heated on a water-bath for half an hour. The colour changed from blue to yellow and the liquid became turbid. It was again heated for 2 hours over a

free flame when the colour changed to reddish brown and a solid mass began to separate out. It was allowed to cool, filtered and washed with water. The compound was insoluble in water, acids, alcohol, methyl alcohol, acetone and ether, difficultly soluble in alkali and highly soluble in pyridine. It could be crystallised from dilute pyridine with much difficulty and the crystals even then were not very well shaped. It melted at 212-214° with decomposition. The yield was 0·5 gm.

(Found : N = 18·7%. C₈H₇N₃, H₂SO₃ requires N = 18·50 per cent.)

Reduction of 1-o-Nitrophenyl-4-phenyl-thiosemicarbazide: Formation of 1-o-Amido-phenyl-4-phenyl-thiosemicarbazide (VI) and 2-Phenylimino-1 : 2 : 3 : 4-tetrahydro-5 : 6-benzo-1 : 3 : 4-triazine (VII).

10 gms. of 1-o-nitrophenyl-4-phenyl-thiosemicarbazide, 10 gms. of granulated tin and 30 c.c. of concentrated hydrochloric acid were heated on a water-bath for 3-4 hours in a flask fitted with an upright condenser. The contents of the flask were then diluted with about 500 c.c. of water and boiled till a pasty semi-solid mass which first formed went in solution. The tin was removed by hydrogen sulphide and the solution concentrated, and on cooling gave (i) white crystals of (VI). These were filtered off and the mother-liquor gave (ii) white curdy precipitate of (VII) on dilution with water.

The white crystalline mass (i) was purified by adding ether to an alcoholic solution of the substance, when it melted at 253-255° with decomposition. It was highly soluble in water and emitted the smell of phenyl-isocyanide when acted upon by nitrous acid. By diazotisation and coupling with β -naphthol, a red azo colour was

produced. The white substance on standing changed to reddish brown. Yield 1·5 gms.

(Found : N = 19·02. C₁₃H₁₄N₄S, HCl requires N = 18·96 per cent.)

The white curdy precipitate (*ii*) was crystallised from dilute alcohol. Yield 0·4 gms. M. p. 150-151°. It was insoluble in water and in alkali but soluble in strong hydrochloric acid. Evidently the hydrochloride is hydrolysed on dilution with water. The compound is feebly basic in nature.

(Found : N = 17·1. C₁₃H₁₁N₃S requires N = 17·4 per cent.)

1-Amidophenyl-4-phenyl-thiosemicarbazide hydrochloride (VI) and Acetic Anhydride.—One gm. of 1-amidophenyl-4-phenylthiosemicarbazide hydrochloride was heated with 3-4 c.c. of acetic anhydride on a sand-bath till a clear solution was obtained. The reaction mixture was poured into cold water when a yellowish white crystalline mass separated out. A second crop was obtained by removing acetic acid by passing steam and evaporating the solution. M. p. 152°. It was insoluble in water and alkali.

o-Nitrophenylhydrazine and Allyl Mustard Oil: Formation of 1-o-Nitrophenyl-4-allylthiosemicarbazide.—An alcoholic solution of 2 gms. of *o*-nitro-phenylhydrazine and 1·5 gm. of allyl mustard oil was heated on a water-bath under reflux for about two hours. The product was poured into water, when yellow shining crystals separated out. These were filtered, washed with water and recrystallised from dilute alcohol. M. p. 164-165°. It was insoluble in water and in mineral acids but soluble in cold dilute alkali, producing a beautiful

bluish violet coloration which vanished on acidification. Yield 2.3 gm.

(Found : N = 22.47. C₁₀H₁₂O₂N₄S requires N = 22.22 per cent.)

The benzaldehyde compound of *o*-nitrophenylhydrazine was prepared according to the method of Bischler (*loc. cit.*).

Reduction of the Benzal derivative of o-Nitrophenylhydrazine : Formation of μ -Phenylbenzimidazole hydrochloride (VIII).

Three gms. of the benzal derivative were heated for 4.5 hours with an excess of tin and hydrochloric acid till a clear colourless solution was obtained, which on cooling gave white needle-shaped crystals. These were further purified by recrystallisation from water slightly acidified with hydrochloric acid. M. p. above 306°. Silver nitrate gave a white precipitate of silver chloride with its aqueous solution. Yield 2 gms.

(Found : N = 12.02. C₁₃H₁₀N₂, HCl requires N = 12.13 per cent.)

μ -Phenylbenzimidazole.—On addition of ammonia to the aqueous solution of 0.3 gm. of the above hydrochloride, a white flocculent mass separated out. It was filtered off and washed with water. Yield 0.2 gm. M. p. 288-289°.

Salicylidene derivative of o-Nitrophenylhydrazine.—A mixture of 6 gm. of *o*-nitro-phenylhydrazine hydrochloride and 6 gm. of salicylaldehyde in dilute alcoholic solution was warmed and shaken. Brilliant crimson-red needle-shaped crystals separated out which were recrystallised from alcohol. M. p. 190°. The

yield was 1 gm. It was insoluble in water, soluble in cold dilute alkali and alcohol. It is a good dye for wool to which it imparts a beautiful orange-red colour from sulphuric acid bath.

(Found : N = 16.51. $C_{13}H_{12}O_3N_3$ requires N = 16.30 per cent.)

The *Benzoyl* derivative.—0.2 gm. of the above compound was "benzoylated by Schotten-Baumann method, when a red solid mass separated which was crystallised from dilute alcohol. M. p. 180° . It was insoluble in alkali.

Our thanks are due to Sir P. C. Ray and Dr. J. C. Ghose for the kind interest they have taken in the work.

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UNIVERSITY OF DACCRA.

Received, April 20, 1925.

Thiodiazines.

Part II.

Condensation of ω -Bromacetophenone with 4-Substituted Thiosemicarbazides. The Constitution of Thiosemicarbazides.

BY

PRAFULLA KUMAR BOSE.

It has been shown in Part I (this *Journal*, 1924, 1, 53) that the condensation of thiosemicarbazide with ω -bromacetophenone leads to the formation of 2-amino-5-phenyl-1 : 3 : 4-thiodiazine and 2-keto-4'-phenyl--2 : 3-dihydro-1 : 3-thiazole hydrazone. It was suggested therein that the formation of the thiazole derivative depended on the basic character of the 4-amino group, the ratios of the yields of the isomers being a measure of the relative basicity of the two extreme amino groups of thiosemicarbazide. A similar conclusion was arrived at by Walther and Roch (*J. pr. Chem.*, 1913, ii, 87, 27) in course of their studies on the condensation of ω -bromacetophenone with substituted thiocarbazides. If this assumption be also true of substituted thiosemicarbazides the relative quantities of the thiazole derivatives obtainable would be expected to be in harmony with the degree of basic strength of the substituted amino group in position 4. It was therefore found desirable to study the condensation of a few 4-substituted thiosemicarbazides with ω -bromacetophenone from a quantitative standpoint with a view to test the hypothesis.

In this communication the condensations of ω -bromoacetophenone with methyl-, ethyl-, allyl-, phenyl-, *p*-tolyl-, *o*-tolyl-, α -naphthyl- and β -naphthyl-thiosemicarbazides are described. The ratios of the yields of thiazoles and the corresponding thiodiazine derivatives are given in the accompanying table.

Nature of substituent.	Ratio of Thiodiazine to Thiazole derivative.	Total yield.
—	1 : 0·2	78 per cent.
Methyl	1 : 1	95 „ „
Ethyl	1 : 0·3*	77 „ „
Allyl	1 : 0·0	90 „ „
Phenyl	1 : 0·18	86 „ „
<i>p</i> -Tolyl	1 : 0·192*	93 „ „
<i>o</i> -Tolyl	1 : 0·8	88 „ „
α -Naphthyl	1 : 0·33	56 „ „
β -Naphthyl	1 : 0·0	81 „ „

If the significance of these ratios be discussed, the above hypothesis will be found inadequate to cover all the facts of experiment. For instance, on the basis of the aforesaid hypothesis the yields of the thiazole derivatives obtained ought to be in the following order :

$\text{Et} > \text{Me} > \text{C}_6\text{H}_5 >$ unsubstituted $> p\text{-C}_6\text{H}_5 > \text{Ph} > o\text{-C}_6\text{H}_5 > \beta\text{-C}_{10}\text{H}_7 > \alpha\text{-C}_{10}\text{H}_7$;

whereas the yields actually obtained are in the order :

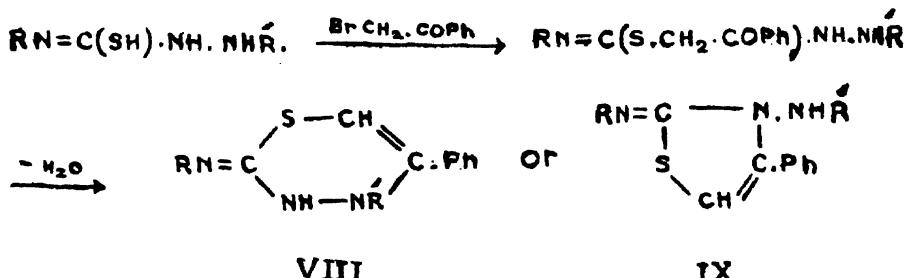
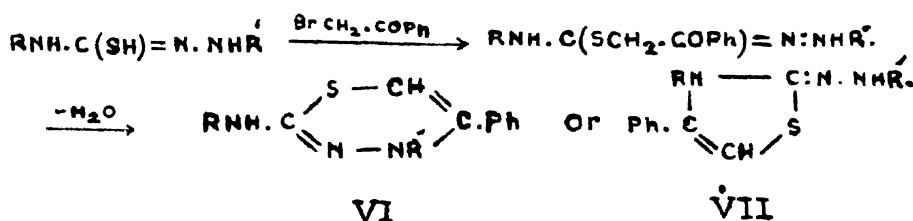
$\text{Me} > o\text{-C}_6\text{H}_5 > \alpha\text{-C}_{10}\text{H}_7 > \text{Et} >$ unsubstituted $> p\text{-C}_6\text{H}_5 > \text{Ph}$.

Clearly then the basic character of the 4-*N* atom partaking in ring-formation cannot be regarded as the sole

* These are only approximate figures.

factor in determining the relative yields of the thiazole derivatives. The author is of opinion that the relative proportions of thioldiazine and thiazole formed in the different cases depend on the relative mobility of the hydrogen atoms attached to the several N-atoms, but at present he has no independent method for measuring mobility. (*Cf.* Usherwood, *Chem. and Ind.*, 1923, 42, 1249).

Substituted thiosemicarbazides of the type RNH.CS.NH.NHR', which can exist in the tautomeric modifications, RNH.C(SH) : N.NHR' (I) or RN : C(SH).NH.NHR' (II), might be expected to react with ω -bromoacetophenone in either of the following ways:—



Of these (VIII) and (IX) are excluded because the products are found to contain no substituted imino groups when tested by methods available for the detection of that group (Berndsen, *Annalen*, 1878, 192, 1; Ber., 1877, 10, 1238; Traumann, *Annalen*, 1888, 249, 43; Walther and Roch, *loc. cit.*).

Moreover the thioldiazines from 4-substituted thiosemicarbazides are not oxidised to cyclic azo-compounds by nitrous acid, amyl nitrite or hydrogen peroxide in glacial

acetic acid as would be expected in the case of a compound (VIII) where R' = H.

1-Acetyl-4-phenylthiosemicarbazide reacts with ω -bromacetophenone to yield an acetyl thiazole which on hydrolysis is converted into the thiazole obtained directly from 4-phenylthiosemicarbazide and the bromo-ketone. Also acetone-4-methylthiosemicarbazone and anisylidene-4-methylthiosemicarbazone react with the bromoketone to give the same thiazole derivatives as are obtained by the action of acetone and anisaldehyde respectively on the thiazole from the bromoketone and 1-methylthiosemicarbazide. These facts justify the author in assigning to substituted thiosemicarbazides the formula $RNH.C(SH) = N.NHR'$ in preference to the tautomeric form (II).

In the previous communication it has been definitely established that thiosemicarbazide reacts in the tautomeric form $NH_2.C(SH) : N.NH_2$ and it appears from the above considerations that 4-substituted thiosemicarbazides, their 1-acetyl derivatives as well as thiosemicarbazones react in an exactly similar manner. (*Cf.* Wilson and Burns, *J. Chem. Soc.*, 1922, 121, 870).

It will be remembered that many reactions of substituted thiosemicarbazides recorded by Freund (*Ber.*, 1890, 23, 2821; 1896, 29, 2483), Marckwald and Bott (*Ber.*, 1896, 29, 2914), Pulvermacher (*Ber.*, 1894, 27, 613), Freund and Meinecke (*Ber.*, 1896, 29, 2511) and others have been based on the form (II). But this assumption is more or less arbitrary and it is interesting to note that the alternative form (I) might as well explain the several reactions without any serious difficulty or disadvantage.

In the previous communication the methylation product of 2-amino-5-phenyl-1 : 3 : 4-thiodiazine was provisionally regarded as 2-methylamino-5-phenyl-1 : 3 : 4-thiodiazine. The latter compound has now been

synthesised from 4-methylthiosemicarbazide and ω -bromoacetophenone and is not identical with the compound previously obtained, which in consequence is now regarded as 2-imino-3-methyl-5-phenyl-2 : 3-dihydro-1 : 3 : 4-thiodiazine. The researches of Pyman (*J. Chem. Soc.*, 1923, 123, 367; *ibid*, 3359) and of other workers also support this conclusion.

The thiodiazines are very stable well-defined substances. They form salts with acids, which, in the case of aryl substituted derivatives, readily hydrolyse in aqueous solution. The alkyl substituted amino thiodiazines are more basic. They decompose slowly when kept in aqueous solutions for a long time. The alkyl-amino thiodiazines are less stable than the aryl-amino ones. On boiling with aqueous alkali or with water slight decomposition occurs and the solution smells of very dilute alkyl or aryl *isonitrile* as the case may be. The isomeric thiazole hydrazones, which are difficult to separate in a pure state from the main product of reaction, are more basic and susceptible to oxidation. The replacement of alkyl groups in position 4 of the thiazole by aryl groups increases stability but decreases the reactivity of the hydrazine group towards ketones and aldehydes. When boiled with alkali they are not affected in the same way as the thiodiazines. Phenyl, *o*-tolyl and *p*-tolyl compounds produce a red or orange precipitate when treated with nitrous acid in hydrochloric acid solution. This property is absent in the α -naphthyl compound. The thiodiazines as already stated are indifferent towards this reagent. It appears that the free amino group of the hydrazine is responsible for the reaction with nitrous acid since the acetyl derivatives or the condensation products of these hydrazones with ketones and aldehydes are not affected by this reagent.

'When 2-phenylamino-5-phenyl-1 : 3 : 4-thiodiazine is boiled with concentrated hydrochloric acid for 3 to 5 hours, it gradually passes into the isomeric thiazole hydrazone. This change which has also been observed with *p*-tolyl- and *o*-tolyl-amino-5-phenyl-1 : 3 : 4-thiodiazines no doubt occurs through the intermediate formation of a *S*-phenacylthiosemicarbazide. Analogous cases in the tetrazine series have been recorded by Bülow (*Ber.*, 1906, 39, 4106) and by Pechmann and Bauer (*Ber.*, 1909, 42, 659).

EXPERIMENTAL.

4-Phenylthiosemicarbazide and ω -Bromacetophenone : Formation of 2-Phenylamino-5-phenyl-1 : 3 : 4-thiodiazine and 2-Keto-3:4-diphenyl-2 : 3-dihydro-1:3-thiazole hydrazone.

Six grams (1 mol.) of ω -bromacetophenone and 5 gms. (1 mol.) of 4-phenylthiosemicarbazide were heated together with 40 c.c. of anhydrous alcohol for 5—10 minutes on the water-bath under reflux. The solution turned dirty red. On cooling 6·5 gms. of prismatic needles melting at 191° were obtained. The mother-liquor on being concentrated gave a further yield of 2·5 gms. (m. p. 191·95°) which under the microscope appeared to consist of two varieties of crystals. The first crop consisted almost entirely of the *hydrobromide* of 2-phenylamino-5-phenyl-1 : 3 : 4-thiodiazine. The second crop was dissolved in absolute alcohol in which it was not very soluble. The solution in the course of two days deposited a mixture of (i) colourless star-like aggregates and (ii) yellow prismatic plates. These were mechanically separated from each other and (ii) was recrystallised from absolute alcohol. It begins to darken at about 206° and melts completely with decomposition between 224-26°. This compound is the *hydrobromide* of

2-keto-3 : 4-diphenyl-2 : 3-dihydro-1 : 3-thiazole hydrazone and was obtained in a yield of about 13% of that required by theory.

Found : N = 12.08.

Calc. for $C_{15}H_{13}N_3SBr$: N = 12.07 per cent.

The hydrobromide was dissolved in a mixture of equal volumes of alcohol and water, filtered and treated with aqueous ammonia when the free base was obtained as colourless needles. It was sparingly soluble in alcohol, acetone or benzene and was recrystallised from dilute pyridine. It begins to char at about 170° and melts completely at 198° with decomposition.

Found : N = 15.84.

Calc. for $C_{15}H_{13}N_3S$: N = 15.73 per cent.

2-Phenylamino-5-phenyl-1 : 3 : 4-thiodiazine was obtained in a similar manner from its hydrobromide. It separates from dilute pyridine in almost colourless needles melting at 175° with decomposition.

Found : N = 15.78 ; S = 11.59 ; C = 67.36 ; H = 5.03.

Calc. for $C_{15}H_{13}N_3S$: N = 15.73 ; S = 11.99 ; C = 67.42 and H = 4.87 per cent.

An aqueous hydrochloric acid solution of this base does not react with nitrous acid whereas the isomeric thiazole compound under the same treatment produces an orange precipitate which is very soluble in ether but almost insoluble in acids or alkalis. It melted at 195-98° with decomposition.

The *acetyl* derivative of the thiodiazine was prepared by boiling the latter with excess of acetic anhydride for one hour. The product was neutralised with sodium carbonate, the residual jelly-like mass was dissolved in

caustic soda, filtered and precipitated by dilute hydrochloric acid. It was repeatedly washed with cold water and dried over sulphuric acid in vacuum. The amorphous powder thus obtained is very soluble in most organic media from which it refuses to separate out in the crystalline state. It melted indefinitely above 110°.

Found: S = 10.32.

Calc. for $C_{17}H_{15}ON_3S$: S = 10.35 per cent.

1-Acetyl-4-phenylthiosemicarbazide.

Finely powdered 4-phenylthiosemicarbazide was covered with an excess of acetic anhydride. The thiosemicarbazide dissolved and immediately solidified with considerable evolution of heat. The product was washed with cold alcohol and recrystallised from hot water in colourless glistening rectangular plates melting at 173°. It is soluble in hot alcohol, glacial acetic acid, pyridine and alkali. From an alkaline solution acids precipitated the original compound in crystalline state.

Found: N = 19.99.

Calc. for $C_9H_{11}ON_3S$: N = 20.09 per cent.

1-Acetyl-4-phenylthiosemicarbazide and ω -Bromacetophenone : Formation of 2-Keto-3 : 4-diphenyl-2 : 3-dihydro-1 : 3-thiazole-acetylhydrazone.

Equimolecular quantities of the components were heated with absolute alcohol for two hours on the water-bath. The solution was evaporated to dryness and the semi-solid residue was thoroughly washed with ether and finally with dry acetone, when small white crystals of the hydrobromide of the above base were obtained. It was dissolved in hot pyridine and the solution was diluted

with water and a little alcohol, when colourless needles were obtained. After recrystallisation it melted at 224°.

Found : C = 64·76 ; H = 5·08.

Calc. for $C_{17}H_{16}ON_3S$: C = 64·65 and H = 5·05 per cent.

It is easily soluble in alcohol, pyridine and chloroform ; sparingly in benzene and acetone. The crystalline substance dissolves slowly in caustic alkalis but readily in dilute acids. From the acid solution the base may be precipitated in the amorphous state by the addition of ammonia or just sufficient caustic soda required to neutralise the acid as excess of the alkali easily dissolves the freshly precipitated base.

Hydrolysis of 2-Keto-3 : 4-diphenyl-2 : 3-dihydro-1 : 3-thiazoleacetylhydrazone.

The acetyl derivative was boiled with an excess of dilute hydrochloric acid for 2-3 hours until an oil began to appear in the solution. It was then cooled, filtered from the small amount of oil and basified with an excess of caustic soda when a white granular precipitate gradually separated out. On crystallisation from a mixture of pyridine and alcohol it was found to melt at 197-98° with decomposition. Its hydrochloric acid solution gave with sodium nitrite an orange precipitate melting at 195-200°. It was identical in other respects with 2-keto-3 : 4-diphenyl-2 : 3-dihydro-1 : 3-thiazole hydrazone obtained in the condensation of ω -bromacetophenone and 4-phenylthiosemicarbazide. A mixture of the two melted at 197°.

Found : C = 67·33 ; H = 5·24.

Calc. for $C_{15}H_{13}N_3S$: C = 67·42 and H = 4·87 per cent.

Acetone-4-phenylthiosemicarbazone.

An acetone solution of 4-phenylthiosemicarbazide was boiled for a few minutes. On cooling and diluting with

water colourless plates of the thiosemicarbazone were obtained. After a second crystallisation from dilute acetone the melting point was found to be 128° .

Found : N = 20.21.

Calc. for $C_{10}H_{18}N_3S$: N = 20.29 per cent,

Acetone-4-phenylthiosemicarbazone and ω -Bromaceto-phenone.

Equimolecular quantities of the components were boiled together in absolute alcohol for 15 minutes. The solution was then evaporated to dryness and the residue was washed with acetone. The hydrobromide was dissolved in dilute alcohol, boiled with animal charcoal and treated with aqueous ammonia when 2-keto-3 : 4-diphenyl-2 : 3-dihydro-1 : 3-thiazole-isopropylidene hydrazone separated in yellow needles. It melted at 165° after two recrystallisations from dilute pyridine.

Found : C = 68.66, 68.29 ; H = 5.73, 5.68.

Calc. for $C_{18}H_{17}N_3S, \frac{1}{2}H_2O$: C = 62.32 ; H = 5.70 per cent.

*Anisylidene-1-phenylthiosemicarbazone.**

It was obtained by boiling an alcoholic solution of 4-phenylthiosemicarbazide and anisaldehyde for a few minutes. From glacial acetic acid it separates in colourless needles melting at 180-181°.

Found : N = 14.79.

Calc. for $C_{15}H_{15}ON_3S$: N = 14.74 per cent.

Anisylidene-4-phenylthiosemicarbazone and ω -Bromaceto-phenone : Formation of 2-Keto-3 : 4-diphenyl-2 : 3-dihydro-1 : 3-thiazole anisylidene hydrazone.

The condensation took place within a few minutes on boiling an alcoholic solution of the components in

* The condensations of free and substituted thiosemicarbazides with various types of ketone and aldehyde are in progress.

equimolecular quantities. The alcoholic solution was treated with pyridine, when the free base appeared in long colourless cottony needles. It was recrystallised from a mixture of pyridine and alcohol when it melted at 161°.

Found : N = 11·13.

Calc. for C₂₃H₁₆ON₃S : N = 10·91 per cent.

The corresponding *benzylidene* compound was similarly obtained from benzylidene-4-phenylthiosemicarbazone and ω -bromacetophenone. It crystallised from dilute pyridine in yellow plates melting at 191°.

Found : N = 11·99.

Calc. for C₂₂H₁₇N₃S : N = 11·83 per cent.

2-Keto-3 : 4-diphenyl-2 : 3-dihydro-1 : 3-thiazolehydrazone and Anisaldehyde.

An alcoholic solution of the reactants was boiled for 2 hours when the condensation product crystallised out from the cold reaction mixture in long colourless needles, and melted at 160·61° after several recrystallisations. It seemed to be identical with the synthetic product described above on the strength of a mixed melting point determination and other physical characteristics. The quantity was too small for analysis.

4-p-Tolylthiosemicarbazide and ω -Bromacetophenone :

***Formation of 4-p-Tolylamino-5-phenyl-1 : 3 : 4-thiodiazine.**

Six gms. of ω -bromacetophenone and 5·4 gms. of the thiosemicarbazide were boiled in absolute alcohol (40 c.c.) for a few minutes. On cooling colourless

needles of the hydrobromide of the above base were obtained. These were collected, washed with acetone and recrystallised from alcohol. The greater portion of the *hydrobromide* was thus obtained in rhombohedra melting at 195°. The isomeric base could not be obtained by the fractional crystallisation of the crude hydrobromide as in the case of the phenyl derivative described before. The mother-liquor after the removal of the thiodiazine hydrobromide was evaporated to dryness and repeatedly extracted with dilute warm hydrochloric acid. The acid extract on being treated with a solution of sodium nitrite gave a crystalline orange-red precipitate which shrank at 110° and melted with decomposition at 138-39°. It resembled the product of interaction of nitrous acid with 2-keto-3 : 4-di-phenyl-2 : 3-dihydro-1 : 3-thiazolehydrazone in general properties.

2-*p*-Tolylamino-5-phenyl-1 : 3 : 4-thiodiazine hydrobromide was dissolved in hot aqueous acetone. On treating with aqueous ammonia the *base* was precipitated in the crystalline state. After several recrystallisations from acetone it was obtained in shining pale-yellow plates melting at 179°.

Found : N = 15.26 ; C = 68.16 ; H = 5.73.

Calc. for $C_{16}H_{15}N_3S$: N = 14.95 ; C = 68.33 and H = 5.34 per cent.

The *acetyl* derivative was obtained in the same way as in the case of the phenyl compound. In solubility and other physical properties it resembled the acetyl derivative of 2-phenylamino-5-phenyl-1 : 3 : 4-thiodiazine. It melted indefinitely above 115°.

Found : N = 12.91 ; S = 10.04.

Calc. for $C_{18}H_{17}ON_3S$: N = 13.01 ; S = 9.91 per cent.

4-o-Tolylthiosemicarbazide and ω -Bromacetophenone:
Formation of 2-o-Tolylamino-5-phenyl-1 : 3 : 4-
thiodiazine and 2-Keto-3-o-tolyl-4-phenyl-
2 : 3-dihydro-1 : 3-thiazole hydrazone.

The condensation was carried out in the same way as in the case of the *p*-tolyl compound. The total yield of the crude hydrobromide amounted to 93.94% of the theoretical of which about 40% appeared to be due to the isomeric thiazole hydrazone. The crude hydrobromide was dissolved in absolute alcohol and left in a crystallising dish for 3-4 days by which time the greater portion of the substance crystallised out in (*i*) small clusters of star-like needles and (*ii*) colourless stout hexagonal crystals. These were mechanically separated and each variety was recrystallised from absolute alcohol. (*i*) Melted at about 206.08° with complete decomposition, while (*ii*) melted at 185° and did not decompose even at 210°. The bases were obtained in pale-yellow needles when pyridine solution of the hydrobromides was diluted with water. The base from (*i*) melted at 136° after several crystallisations from dilute pyridine and gave the characteristic orange-red precipitate with nitrous acid. Evidently this compound is 2-Keto-3-o-tolyl-4-phenyl-2 : 3-dihydro-1 : 3-thiazole hydrazone.

Found : N = 15.15.

Calc. for C₁₆H₁₅N₃S : N = 14.95 per cent.

The thiodiazine from (*ii*) was repeatedly crystallised from acetone until the melting point rose to 148°. It is sparingly soluble in benzene or alcohol and almost insoluble in ether.

Found : C = 68.60 ; H = 5.85.

Calc. for C₁₆H₁₅N₃S : C = 68.33 ; H = 5.34 per cent.

**2-o-Tolylamino-5-phenyl-1 : 3 : 4-thiodiazine
and Bromine.**

The action of bromine on the phenyl and *p*-tolyl compounds resulted in the formation of tarry products from which no definite compounds could be isolated. In the case of the *o*-tolyl compound, however, a *monobromo* derivative was obtained as follows: Molecular proportions of the reactants in glacial acetic acid solution were mixed in the cold. The solution was diluted with water after some time and neutralised with sodium carbonate. The white solid, which gradually appeared, was crystallised from pyridine and finally from acetone in minute crystals which melted at 155-56°.

Found: N = 11.74; Br = 22.02.

Calc. for C₁₆H₁₄N₃SBr: N = 11.67; Br = 22.22 per cent.

*Allylthiosemicarbazide and ω -Bromacetophenone:
Formation of 2-Allylamino-5-phenyl-1 : 3 : 4-thiodiazine.*

The condensation product was isolated in about 90% of the theoretical yield as the *hydrobromide*, which crystallised from alcohol in stout rectangular plates melting at 165°. The base was obtained from a cold aqueous solution of the hydrobromide by treatment with a slight excess of aqueous ammonia or dilute sodium carbonate. The greenish yellow plates, which separated out, were collected after 2 to 3 hours, washed with cold water and dried over porous porcelain. For purification a benzene solution of the base was diluted with 4-6 times its volume of petrol ether when the thiodiazine separated in long colourless needles melting at 99°.

Found: N = 18.55.

Calc. for C₁₂H₁₈N₃S: N = 18.26 per cent.

It is very soluble in alcohol, acetone, benzene, pyridine and chloroform, less soluble in ether and sparingly in petrol ether. It seems that the isomeric base is not produced in this condensation since all attempts to isolate it as the benzylidene or anisylidene derivative from the crude hydrobromide or from the mother-liquor left after the separation of the latter have been futile.

**4-a-Naphthylthiosemicarbazide and ω -Bromacetophenone :
Formation of 2-a-Naphthylamino-5-phenyl-1 : 3 : 4-thiodiazine and 2-Keto-3-a-naphthyl-4-phenyl-2 : 3-dihydro-1 : 3-thiazole hydrazone.**

a-Naphthylthiosemicarbazide (2.17 gms.) and the bromoketone (2 gms.) were boiled for a few minutes with 30 c. c. of dry ethyl alcohol. On cooling the hydrobromides of the above-mentioned bases crystallised out from the reaction mixture in 56% of the theoretical yield. On recrystallisation from alcohol a mixture of two varieties of well-defined crystals was obtained: (i) colourless rectangular needles (1.75 gms.), which softened at 203° and melted at 220° with decomposition, and (ii) pale yellowish-brown rhombic crystals (0.45 gm.) melting at 208° with evolution of gases. These were mechanically separated. The thiodiazine was obtained from (i) by treating its aqueous-alcoholic solution with ammonia. It crystallised from alcohol in yellow needles. After three crystallisations the melting point remained constant at 166-67°.

Found : N = 13.55 ; S = 10.08.

Calc. for C₁₉H₁₅N₃S : N = 13.25 ; S = 10.09 per cent.

* The isomeric base was obtained in a similar manner from (ii). It crystallised from alcohol in pale greenish yellow needles melting at 179°.

Found : C = 71.88 ; H = 5.02.

Calc. for C₁₉H₁₅N₃S : C = 71.92 ; H = 4.73 per cent.

The *acetyl* derivative of the above thiodiazine, obtained by the action of acetic anhydride on the base, is a white amorphous powder which closely resembles the *acetyl* derivatives already described.

Found : S = 8.53.

Calc. for $C_{21}H_{17}ON_3S$: S = 8.89 per cent.

2- β -Naphthylamino-5-phenyl-1 : 3 : 4-thiodiazine.

It was obtained from β -naphthylthiosemicarbazide and ω -bromacetophenone by an identical method. The hydrobromide was isolated in 76% yield of that required by theory. It was dissolved in pyridine and on dilution with water the solution quickly deposited beautiful yellow plates of the base. These were thrice recrystallised from dilute pyridine in pale-yellow plates or needles which melted at 153° . No trace of the isomer could be detected.

Found : N = 13.52.

Calc. for $C_{19}H_{15}N_3S$: N = 13.25 per cent.

4-Methylthiosemicarbazide and ω -Bromacetophenone : Formation of 2-Methylamino-5-phenyl-1 : 3 : 4-thiodiazine and 2-Keto-3-methyl-4-phenyl-2 : 3-dihydro-1 : 3-thiazole-isopropylidene hydrazone.

2.62 Gms. of 4-methylthiosemicarbazide and 5 gms. of the bromo-ketone were digested with 30 c.c. of dry ethyl alcohol for 15 minutes. Alcohol was then distilled off when a dark oil remained behind. It was washed with ether and was then heated with about 20 c.c. of acetone when a dirty white crystalline product was obtained. This was collected and was washed with dry acetone. It is a mixture of the hydrobromides of the above two bases.

This was dissolved in warm water, filtered and the filtrate treated with an excess of sodium carbonate solution. The yellow crystalline product which separated out, was collected after 2-3 hours, washed well with water and dried in a vacuum (5·2 gms.). It was then dissolved in hot benzene, filtered and diluted with twice its volume of petrol ether, when *2-methylamino-5-phenyl-1 : 3 : 4-thiodiazine* was obtained as cream-coloured needles (2·4 gms.), which after two recrystallisations from benzene melted at 144-45°. It is freely soluble in alcohol, pyridine or dilute acids but almost insoluble in ligroin.

Found : N = 20·83 ; C = 58·56 ; H = 5·90.

Calc. for $C_{10}H_{11}N_3S$: N = 20·49 ; C = 58·63 and H = 5·37 per cent.

The isopropylidene derivative of the isomeric base was obtained as follows: The benzene-ligroin mother-liquor was evaporated to dryness, the residue was pressed on porous plate to remove some adhering oil and crystallised from dilute methyl alcohol in yellow plates which melted at 92-93°. It is very soluble in most organic solvents as well as in dilute acids. The synthetic product from acetone-4-methylthiosemicarbazone and ω -bromacetophenone (*vide infra*) melted at 92·5° and a mixture of these two did not alter the melting point.

Found : N = 17·17.

Calc. for $C_{13}H_{15}N_3S$: N = 17·14 per cent.

2-Keto-3-methyl-4-phenyl-2 : 3 dihydro-1 : 3-thiazole-anisylidene hydrazone.

In another experiment the reaction product of 4-methyl thiosemicarbazide and ω -bromacetophenone was treated with anisaldehyde in hot alcoholic solution. On

cooling yellowish needles of the hydrobromide of the above base were obtained. An aqueous-alcoholic solution of the salt on treatment with ammonia gave bright yellow plates of the base which after several crystallisations from pyridine melted at 128°. It appeared to be identical with the synthetic product (*vide infra*). Mixed m. p. 127-28°.

Found : N = 13.15.

Calc. for $C_{18}H_{11}ON_3S$: N = 13.00 per cent.

Acetone-4-methylthiosemicarbazone.

It is easily obtained by boiling 4-methylthiosemicarbazide in acetone solution for a few minutes. From dilute alcohol it separates in colourless needles melting at 118°.

Found : N = 29.22.

Calc. for $C_5H_{11}N_3S$: N = 28.97 per cent.

Acetone-4-methylthiosemicarbazone and ω -Bromacetophenone : Formation of 2-Keto-3-methyl-4-phenyl-2 : 3-dihydro-1 : 3-thiazole isopropylidene hydrazone.

Equimolecular quantities of the components were boiled together for a few minutes in acetone solution. The reaction begins with evolution of much heat and colourless needles of the hydrobromide separate out (m. p. 208-09°). These were dissolved in 80% methyl alcohol, filtered and treated with an excess of aqueous ammonia. The crystalline yellow plates of the base after two or three recrystallisations from dilute methyl alcohol melted at 92.5°.

Found : C = 63.40 ; H = 6.14.

Calc. for $C_{18}H_{15}N_3S$: C = 63.67 and H = 6.13 per cent.

Anisylidene-4-methylthiosemicarbazone and its Condensation with ω -Bromacetophenone.

Anisylidene-4-methylthiosemicarbazone, from anisaldehyde and 4-methylthiosemicarbazide, crystallises from a mixture of pyridine and alcohol in colourless shining plates melting at 207°. Like acetone-4-methylthiosemicarbazone it possesses acid properties.

Found : N = 18·82.

Calc. for $C_{10}H_{13}ON_3S$: N = 18·83 per cent.

It was condensed with the bromo-ketone in the usual manner. The *hydrobromide* of the base decomposed and melted at 235-36°. The free *base* crystallised from pyridine in yellow shining plates, which melted at 127-28°.

4-Ethylthiosemicarbazide and ω -Bromacetophenone: Formation of 2-Ethylamino-5-phenyl-1 : 3 : 4-thiodiazine and 2-Keto-3-ethyl-4-phenyl-2 : 3-dihydro-1 : 3-thiazole-isopropylidene Hydrazone (?).

The procedure was similar to that of the methyl compound. The thiodiazine crystallised from benzene or dilute alcohol in colourless needles melting at 158°. It is very soluble in pyridine, less soluble in alcohol or acetone and almost insoluble in petrolether. Yield 2·7 gms. from 2·38 gms. of 4-ethylthiosemicarbazide.

Found : N = 19·24; C = 60·30; H = 6·04.

Calc. for $C_{11}H_{15}N_3S$: N = 19·18; C = 60·29 and H = 5·93 per cent.

The reddish brown mother-liquor (benzene), after the separation of the thiodiazine, was evaporated to dryness when a red oil was obtained. It was dissolved in dilute

methyl alcohol and treated with dilute hydrochloric acid. The clear acid solution when treated with ammonia gave a small quantity of a brown oil which gradually solidified and was probably the acetone condensation product of the isomer (.8 gm.). It could not be sufficiently purified for analysis.

*The Action of Concentrated Hydrochloric Acid on
2-Phenyl-(*p*-Tolyl- or *o*-Tolyl)-amino-5-phenyl-1:3:4-thiodiazine.*

The thiodiazine was boiled with concentrated hydrochloric acid for 3 to 5 hours. The solution was cooled, filtered from a heavy oil which had formed and treated with an excess of caustic soda. A white precipitate gradually made its appearance. On crystallisation from pyridine it melted at 197° with decomposition. It gave the characteristic orange precipitate with nitrous acid and its identity with 2-keto-3:4-diphenyl-2:3-dihydro-1:3-thiazole hydrazone was further established by a mixed melting point determination. Similar results were obtained with *p*- and *o*-tolyl derivatives.

My best thanks are due to Sir P. C. Ray for his keen interest and encouragement during the investigation.

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The Influence of Electrolytes on the Solubilities of Some Organic Acids.

* By

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It is well known that addition of small quantities of electrolytes and non-electrolytes influences the solubilities of various substances in water. Hans Ellen (*Zeit. physikal. Chem.*, 1899, 30, 360) and Rothamind (*Zeit. physikal. Chem.*, 1900, 33, 401) are among the recent investigators on the subject. Hoffmann and Lengbeck (*Zeit. physikal. Chem.*, 1905, 51, 385) found that the solubilities of organic acids were remarkably increased by the addition of small amounts of electrolytes but non-electrolytes produced no appreciable effect. The relative magnitude of the influence of the anions and cations of a few electrolytes was investigated by Max Levin (*Zeit. physikal. Chem.*, 1906, 56, 513), but no systematic study was made by him as well. Later on Bronsted (*J. Am. Chem. Soc.*, 1920, 42, 1448 *et seq.*) and Sidgwick and his pupils (*J. Chem. Soc.*, 1923, 123, 2819 *et seq.*), have studied the influence of orientation on the solubilities of different substances and also tried to explain the phenomenon of solubility.

In order to investigate the phenomenon more fully the authors have tried to make exhaustive study of the influence of various electrolytes as such and that of their anions and cations at varying concentrations and temperatures. Also they have examined whether the

behaviour shown by the acids as regards the solubilities in water is characteristic of the nature of the acids used, or is affected by their orientation and composition.

EXPERIMENTAL.

The acids used in the investigation were *o*-nitrobenzoic acid, *m*-nitrobenzoic acid, *p*-nitrobenzoic acid, *p*-aminobenzene sulphonic acid and *p*-hydroxybenzene sulphonic acid. The electrolytes selected were the sulphates, chlorides and nitrates of calcium, strontium and barium. The sulphates of the last three metals could not be tried as they are not soluble in water. The acids used were either "Merck's re-crystallized" or were prepared by the usual methods from the corresponding substances and purified by the standard methods. Other chemicals used throughout the investigation were "Becker's Purified Chemicals" of 99.998 per cent. purity. In this piece of research the purity of the chemicals and the cleanliness of the apparatus is of utmost importance as the solubilities are greatly affected by the presence of even traces of foreign substances. Scrupulous care was therefore taken in this direction. The apparatus was previously calibrated by the standard methods. The temperature of the thermostat was regulated by a mercury-toluene thermo-regulator.

A saturated solution of the acid under investigation was prepared in re-distilled water at 10 degrees above the temperature at which the solubilities were measured. When the solution was ready, 100 c.c. of this were transferred to each flask by means of a pipette (previously calibrated for that temperature) containing accurately weighed quantities of various electrolytes. The flasks were then corked and placed in the thermostat regulated at the temperature at which the solubilities were determined.

RELATIVE SOLUBILITIES OF THE ACIDS

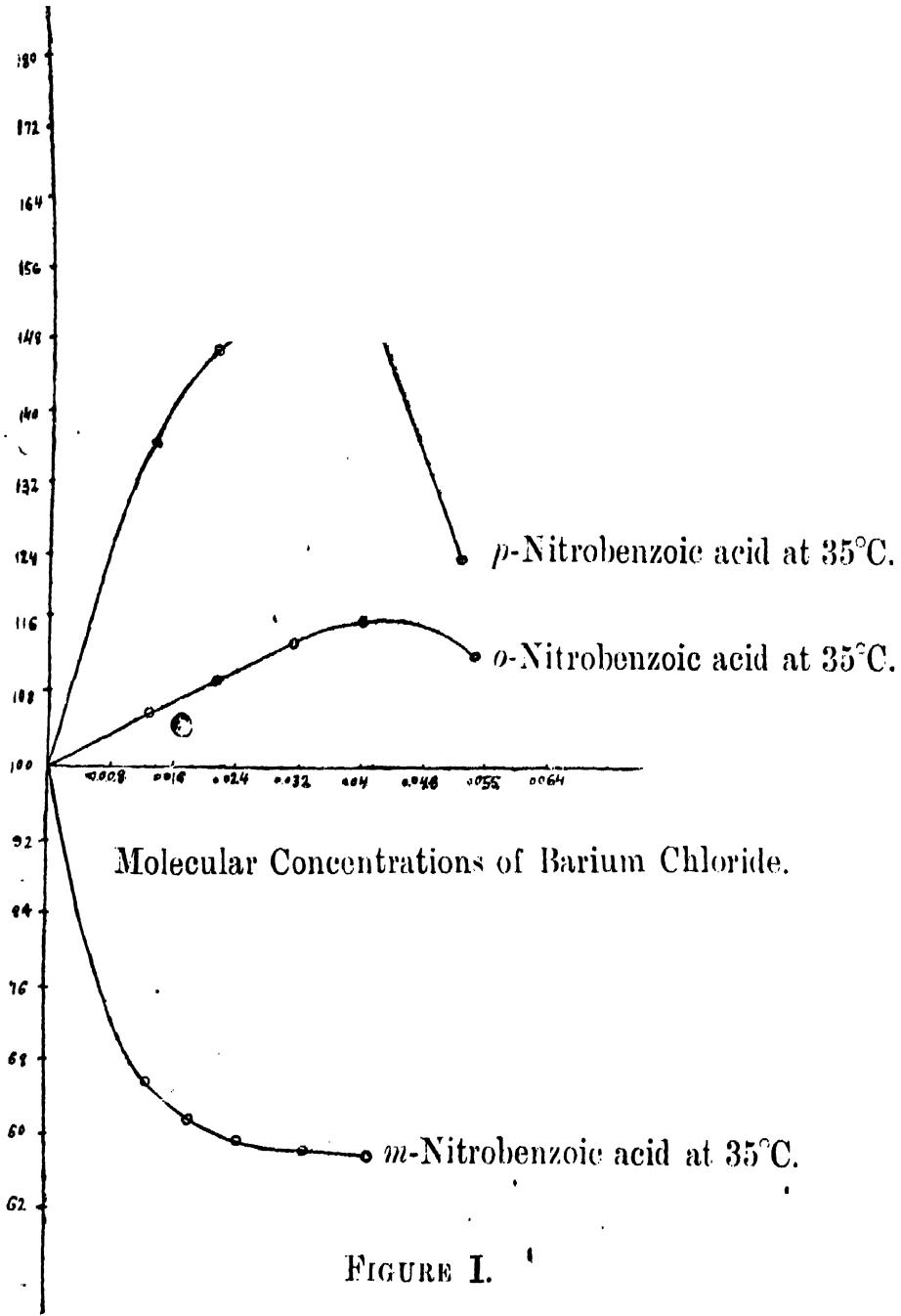


FIGURE I.

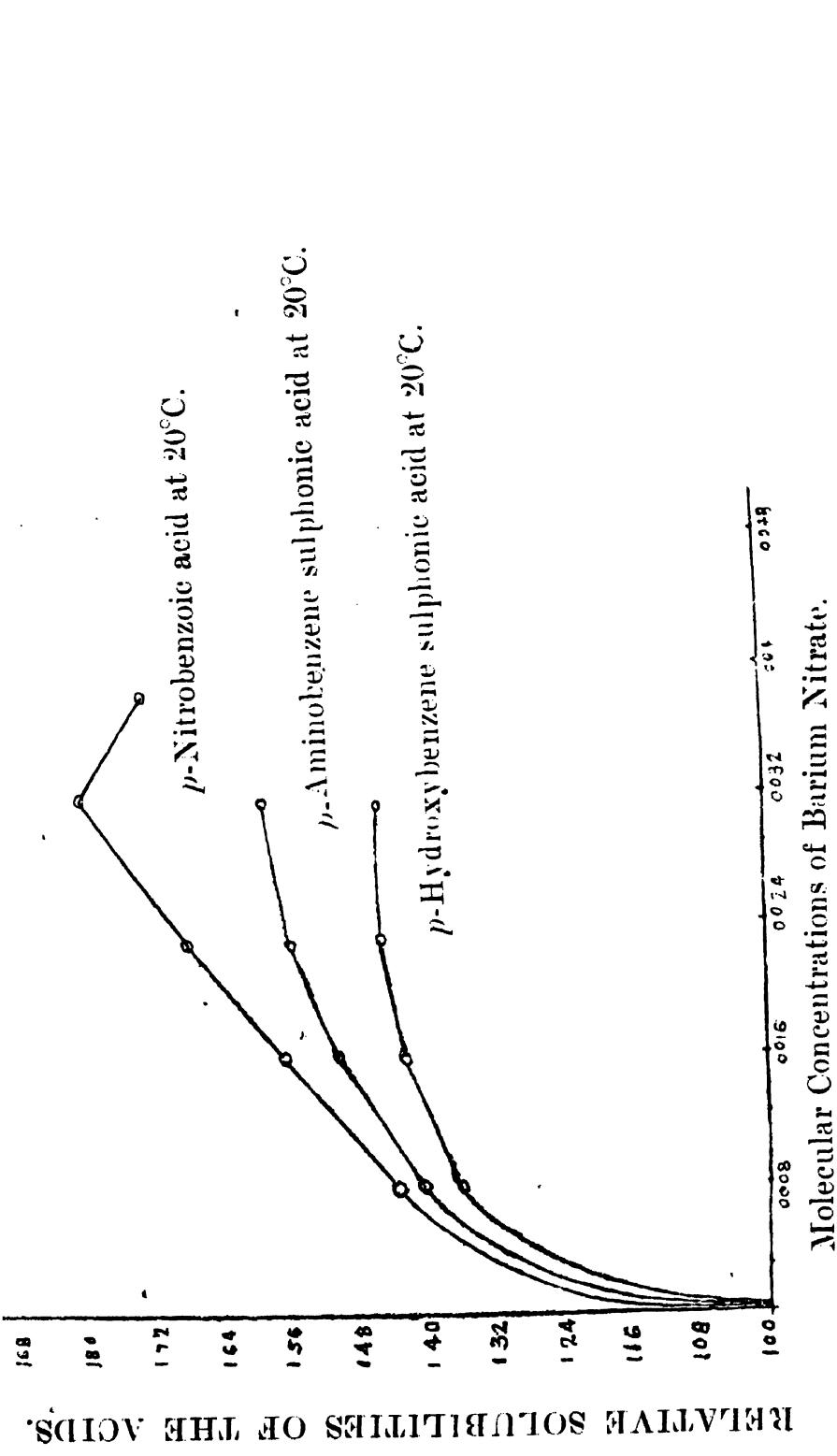
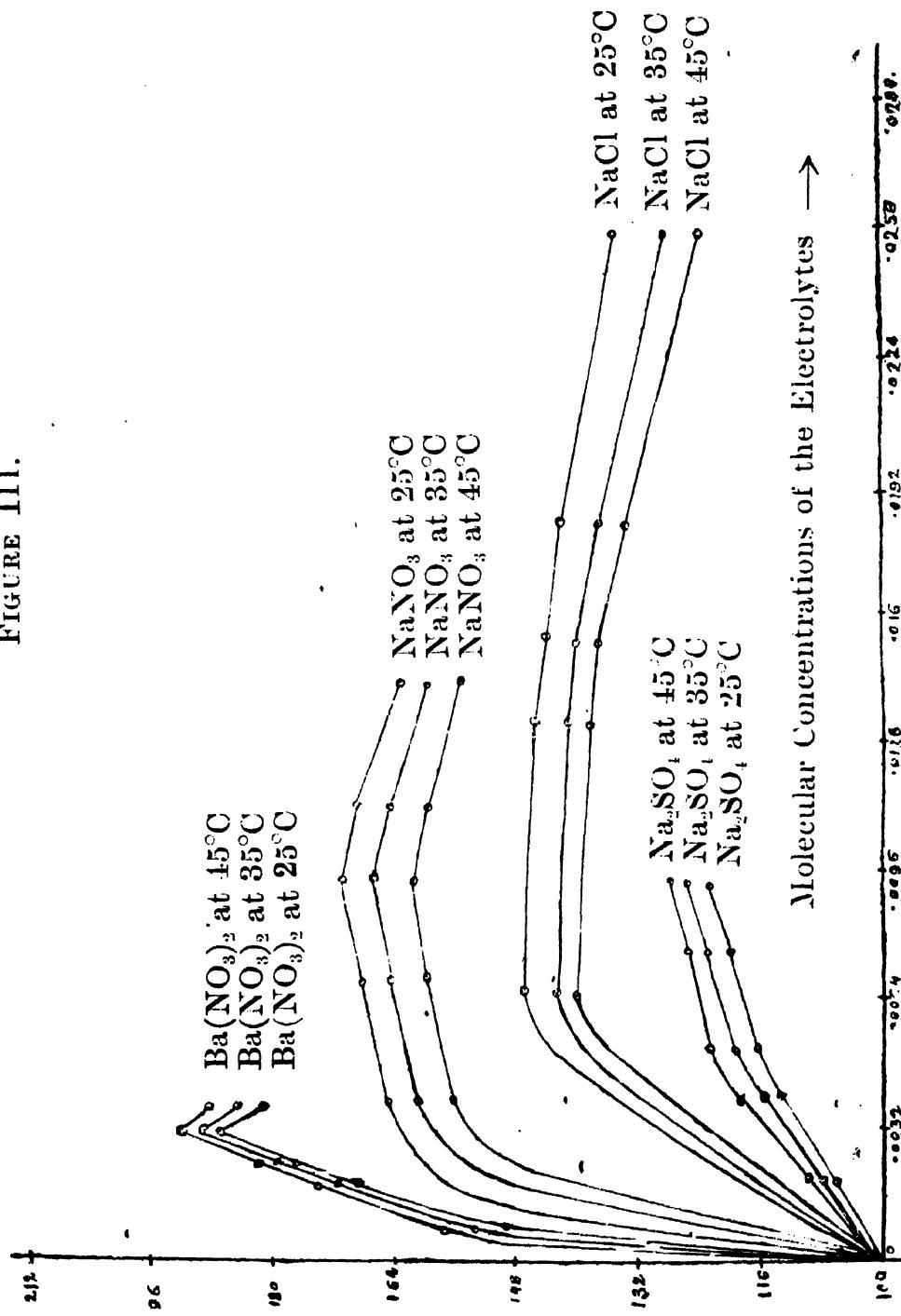


FIGURE II.

RELATIVE SOLUBILITIES OF THE ACIDS.

FIGURE III.



The solubilities were measured at three temperatures, 45°C, 35°C and 25°C in the case of the nitrobenzoic acids and at 40°C, 30°C and 20°C in the case of the sulphonic acids. In each case the temperature of the thermostat was carefully adjusted and the flasks were kept there for sufficient time to attain the temperature of the bath before the readings were taken. The solubilities were then determined by titrating the acid against standard alkali.

The solubilities of the acid in the absence of the electrolytes are taken to be 100—an arbitrary standard—and the solubilities of the acids in presence of varying amounts of the electrolytes are referred to that standard. Curves have been drawn with concentrations of the electrolytes and the solubilities as co-ordinates for various electrolytes and some of them are shown in Figures I, II and III.

In order to make a comparative study of the various electrolytes, their effect on the solubilities of *o*-nitrobenzoic, *m*-nitrobenzoic and *p*-nitrobenzoic acids was studied with the same molecular concentration of the electrolytes and at the same temperature and is described in Table IV.

Note.—Original solubilities of the nitrobenzoic acids under investigation as determined by the authors:—

	25°C.	35°C.	42°C.	
<i>Ortho</i> acid	... 0·750	1·30	2·28 per 100 gms. of water.	
<i>Meta</i> acid	... 0·344	0·418	0·515	„
<i>Para</i> acid	... 0·028	0·025	0·022	„
Solubilities of <i>p</i> -aminobenzene sulphonic acid at 20°C. 30°C. 40°C.				„
	1·00	1·45	1·91	„

Temperature = 35° C.

TABLE I.

o-Nitrobenzoic Acid.

Electrolyte used.	Molecular concentration.	Actual solubilities of the acid in 100 gms. of water.	Relative solubility of the acid.	Electrolyte used.	Molecular concentration.	Actual solubilities of the acid in 100 gms. of water.	Relative solubility of the acid.	Electrolyte used.	Molecular concentration.	Actual solubilities of the acid in 100 gms. of water.	Relative solubility of the acid.
Ammonium Sulphate	·0000	1·300	100·00	Ammonium Chloride	·0000	1·300	100·00	Ammonium Nitrate	·0000	1·300	100·00
	·0016	1·245	95·79		·0040	1·256	96·58		·0028	1·313	101·03
	·0030	1·222	94·03		·0058	1·227	94·42		·0046	1·332	102·47
	·0050	1·191	91·58		·0079	1·199	92·26		·0062	1·337	103·87
	·0067	1·163	89·47		·0094	1·193	91·81		·0078	1·298	99·36
	·0082	1·136	87·36		·0117	1·171	89·80		·0093	1·252	96·32
	·0000	1·300	100·00	Sodium Chloride	·0000	1·300	100·00	Sodium Nitrate	·0000	1·300	100·00
	·0014	1·295	99·65		·0041	1·241	95·44		·0026	1·318	101·40
	·0033	1·232	94·74		·0058	1·186	91·23		·0050	1·314	101·05
	·0053	1·154	88·58		·0094	1·126	86·66		·0077	1·297	99·79
Potassium Sulphate	·0071	1·039	83·85		·0131	1·068	82·11		·0113	1·277	97·89
	·0078	1·072	82·46		·0155	1·040	80·00		·0137	1·250	96·14
	·0000	1·300	100·00	Potassium Chloride	·0000	1·300	100·00	Potassium Nitrate	·0000	1·300	100·00
	·0015	1·310	100·70		·0031	1·228	94·49		·0028	1·391	107·02
Potassium Sulphate	·0020	1·254	96·49		·0053	1·213	93·33		·0052	1·355	104·25

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•0045	1.098	84.21	•0088	•1.149	88.42	1.272	97.84
•0071	0.981	75.43	•0112	1.024	78.77	1.231	94.68
			•0000	1.3000	100.00	1.300	100.00
			•0015	1.334	102.59	1.715	131.93
			•0028	1.364	104.91	1.688	129.32
			•0052	1.878	105.96	1.629	125.33
			•0059	1.332	102.46	1.616	123.51
			•0075	1.213	93.33	1.570	120.71
			•0000	1.300	100.00	1.300	100.00
			•0012	1.330	102.29	1.783	137.19
			•0021	1.365	105.02	1.752	134.74
			•0029	1.416	108.96	1.711	131.58
			•0040	1.464	112.63	1.676	128.92
			•0051	1.419	109.12	1.610	123.80
			•0000	1.300	100.00	1.300	100.00
			•0012	1.388	106.80	1.830	140.70
			•0021	1.420	109.21	1.788	137.54
			•0031	1.485	114.23	1.754	134.90
			•0040	1.510	116.14	1.677	128.22
			•0055	1.454	112.63	1.570	122.06

TABLE II.

m-Nitrobenzoic Acid.

Temperature = 35° C.

Electrolyte used.	Molecular concentration.	Actual solubilities of the acid in 100 grms. of water.	Relative solubility of the acid.	Electrolyte used.	Molecular concentration.	Actual solubilities of the acid in 100 grms. of water.	Relative solubility of the acid.	Electrolyte used.	Molecular concentration.	Actual solubilities of the acid in 100 grms. of water.	Relative solubility of the acid.
Ammonium Sulphate	.0000	.418	100.00	Ammonium Chloride	.0000	.418	100.00	Ammonium Nitrate	.0000	.418	100.00
	.0017	.3105	76.70		.0036	.2043	48.88		.0028	.2189	52.37
	.0030	.2593	64.44		.0080	.1950	46.66		.0038	.1718	41.11
	.0048	.2616	62.59		.0078	.1805	45.35		.0049	.1533	37.41
	.0064	.2554	61.11		.0100	.1830	43.70		.0069	.1315	31.48
	.0097	.2446	58.52		.0148	.1672	40.00		.0082	.1160	27.77
Sodium Sulphate	.0000	.418	100.00	Sodium Chloride	.0000	.418	100.00	Sodium Nitrate	.0000	.418	100.00
	.0020	.3235	77.41		.0070	.2059	49.26		.0016	.2199	52.63
	.0032	.2848	68.15		.0088	.1943	45.55		.0032	.1842	44.07
	.0051	.2771	66.30		.0125	.1718	41.11		.0057	.1625	38.88
	.0072	.2687	64.30		.0171	.1485	35.55		.0078	.1449	34.44
	.0089	.2616	62.59		.0237	.1223	29.26		.0101	.1254	30.00
Potassium Sulphate	.0000	.418	100.00	Potassium Chloride	.0000	.418	100.00	Potassium Nitrate	.0000	.418	100.00
	.0016	.3317	79.37		.0033	.2337	55.93		.0017	.2548	60.96
	.0027	.2987	71.48		.0075	.2213	52.96		.0032	.1996	47.77

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Calcium Chloride	•0116	70.74	•2060	69.00	•0052	1780	42.59
	•0048	•2910	69.68	•1991	47.41	•0071	1563
	•0063	•2848	68.15	•0197	44.44	•0058	37.41
				•0000	100.00	•0000	33.70
				•418	100.00	•418	100.00
Calcium Nitrate	•0023	•2525	69.41	•0000	•0016	•2427	58.07
	•0038	•2365	56.66	•0000	•0033	•2290	54.80
	•0058	•2291	54.81	•0000	•0043	•2215	53.01
	•0095	•2229	53.33	•0000	•0050	•2187	52.33
	•0113	•2133	57.48	•0000	•0035	•2161	51.71
Sodium Chloride	•0000	•418	100.00	•0000	•0000	•418	100.00
	•0010	•2350	63.41	•0000	•0012	•2363	56.55
	•0017	•2430	58.15	•0000	•0023	•2284	54.66
	•0025	•2384	57.04	•0000	•0028	•2244	53.70
	•0039	•2348	56.19	•0000	•0050	•2161	51.70
	•0040	•2270	54.33	•0000	•0031	•2140	51.22
Barium Chloride	•0000	•418	100.00	•0000	•0000	•418	100.00
	•0013	•2375	64.00	•0000	•0013	•2343	56.06
	•0018	•2523	60.37	•0000	•0018	•2336	56.90
	•0024	•2445	58.52	•0000	•0024	•2290	54.80
	•0033	•2399	57.41	•0000	•0033	•2235	53.49
	•0041	•2368	56.46	•0000	•0041	•2202	52.70*

TABLE III.

*p-Nitrobenzoic Acid.*Temperature = 35°C

Electrolyte used.	Molecular concentration.	Actual solubilities of the acid in 100 gms. of water.	Relative solubility of the acid.	Electrolyte used.	Actual solubilities of the acid in 100 gms. of water.	Relative solubility of the acid.	Electrolyte used.	Molecular concentration.	Actual solubilities of the acid in 100 gms. of water.	Relative solubility of the acid.	
Ammonium Sulphate	.000.0	.025	100.00	Ammonium Chloride	.0000	.025	100.00	Ammonium Nitrate	.0000	.025	100.00
	.0031	.027	109.60		.0052	.0346	138.54		.0047	.0402	160.69
	.0042	.028	110.69		.0084	.0353	141.23		.0085	.0413	165.08
	.0087	.029	117.62		.0103	.0352	140.92		.0103	.0414	165.77
	.0102	.0295	117.85		.0137	.0343	137.31		.0137	.0405	162.08
	.0125	.029	116.54		.0178	.0320	128.00		.0165	.0386	168.38
Sodium Sulphate	.0000	.025	100.00	Sodium Chloride	.0000	.025	100.00	Sodium Nitrate	.0000	.025	100.00
	.0018	.0269	107.77		.0035	.0358	143.38		.0036	.0405	162.00
	.0040	.0289	115.46		.0135	.0655	142.08		.0070	.0417	164.69
	.0051	.0306	120.15		.0152	.0353	141.36		.0094	.0418	167.38
	.0076	.0309	123.85		.0184	.0347	138.68		.0112	.0413	165.28
	.0102	.0315	126.04		.0257	.0324	129.85		.0144	.0401	166.77
Potassium Sulphate	.0000	.025	100.00	Potassium Chloride	.0000	.025	100.00	Potassium Nitrate	.0000	.025	100.00
	.0017	.0272	108.77		.0035	.0328	131.38		.0028	.0396	158.50
	.0027	.0281	112.46		.0049	.0342	137.08		.0052	.0414	165.69

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•0047	•0288	115.15	•0079	144.38	•0078	•0423	169.38
•0063	•0295	117.85	•0096	•0359	143.68	•0111	•0420
•0084	•0300	120.04	•0143	•0050	140.04	•0122	•415
				Calcium Chloride	•0000	100.00	100.00
				•0027	•0348	139.38	•0000
				•0034	•0352	141.08	•0022
				•0067	•0323	129.46	•0036
				•0088	•0283	113.23	•0050
				•0092	•0276	111.54	•0063
				Strontium Chloride	•0000	100.00	100.00
				•0013	•0341	136.38	•0014
				•0024	•0350	142.56	•0023
				•0035	•0366	146.67	•0031
				•0047	•0339	135.92	•0049
				•0055	•0298	119.52	•0068
				Radium Chloride	•0000	•025	100.00
				•0013	•0339	135.84	•0000
				•0021	•0363	145.37	•0008
				•0037	•0382	163.06	•0023
				•0041	•0370	148.00	•0032
				•0053	•0311	124.58	•0037
							•0461
							184.48

TABLE IV.

Comparative solubilities of the nitrobenzoic acids containing the same groups in different positions under the same conditions.

Molecular concentration = .0011. Temperature 35°C.

Electrolyte used.		<i>o</i> -Nitro-benzoic acid.	<i>m</i> -Nitro-benzoic acid.	<i>p</i> -Nitro-benzoic acid.
Ammonium Sulphate	...	97·0	94·2	103·0
Ammonium Chloride	...	99·0	87·0	107·6
Ammonium Nitrate	...	100·4	81·7	114·0
Sodium Sulphate	...	98·9	91·2	104·2
Sodium Chloride	...	99·4	86·8	107·9
Sodium Nitrate	...	100·9	76·9	118·6
Potassium Sulphate	...	100·1	85·0	105·2
Potassium Chloride	...	100·5	84·5	109·9
Potassium Nitrate	...	102·8	75·5	125·0
Calcium Chloride	...	101·3	81·4	115·9
Calcium Nitrate	...	120·4	71·9	149·0
Strontium Chloride	...	102·3	65·4	128·0
Strontium Nitrate	...	125·7	63·7	150·4
Barium Chloride	...	106·2	62·4	129·6
Barium Nitrate	...	109·0	61·8	157·7

Discussion of Results.

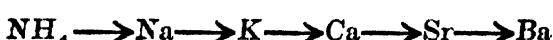
A reference to the tables and graphs shows that the addition of electrolytes has a marked effect on the solubilities of these organic acids. There is a marked regularity in the decrease or increase of the solubilities as the concentration of the electrolytes is increased. The various conclusions that may be drawn from the foregoing experiments may be briefly stated as follows:

1. *The Influence of Temperature.*—With the increase in temperature, the influence of the nitrates and chlorides of alkali metals in increasing or decreasing the solubilities of the acids decreases, but that of the nitrates and chlorides of the alkaline earth metals increases as the temperature rises. These observations are clearly shown in the case of *p*-nitrobenzoic acid in Figure III. Similar curves were obtained in the case of other acids as well. The solubility of the *meta*-acid in the presence of electrolytes does not show much variation with the change in temperature. But in general there is an increase in the solubilities of the acids with the rise in temperature.

2. *The Influence of Electrolytes.*—The solubilities of the *ortho*- and *para*-acids first increase with the increase in the concentrations of the electrolytes used, reach a maximum and then decrease with the increasing concentrations (*cf.* Graphs I and II). The maximum increase in the solubility of the acids is different with different electrolytes. The solubility of the *meta*-acid decreases first rapidly, and then slowly and regularly as the concentration of the electrolytes is raised.

3. *The Influence of the Basic Radicles.*—The basic radicles of the electrolytes show an extraordinary regularity in their effect on the solubility of the acid. As the

atomic weight of the basic radicles of the electrolytes increases, there is an increase in their effect on the solubility of the acids as well. The same influence is observed in the case of *meta*-acid, but instead of increase there is a decrease in the solubility in the same order. The various basic radicles employed may, therefore, be represented in order of their influence on the solubilities of the acids as follows :



This order is the same as that of their atomic weights. From this we may conclude that the divalent positive radicles have a greater influence than the monovalent ones.

4. *The Influence of the Negative Radicles.*—The negative radicles of the various electrolytes also seem to exert a definite effect on the solubility. The effect of the nitrates of different metals on the increase in the solubilities of the acids is far greater as compared to the effect exerted by the corresponding chlorides in the same molecular concentration. Similarly the effect of the chlorides is greater than that of the sulphates. Thus the order of the groups of acid radicles with regard to the increase of the solubility may be written as



The *meta*-acid is also influenced by the acid radicles in the same order—the nitrates decreasing the solubilities of the acid most and the sulphates least, the chlorides standing between the two.

5. *The Influence of the Orientation of the Acid.*—From the tables and graphs we find that the orientation of the acids plays an important part in the effect produced in their solubilities by various electrolytes. The effect of the addition of electrolytes on the solubilities of the

ortho- and the *para*-acids is similar to one another, but the maxima obtained in the case of the *para*-acids have higher values to those obtained in the case of *ortho*-acids. The *meta*-acid on the contrary shows quite abnormal results as compared to the *ortho*- and the *para*-acids. In the case of the *ortho*- and *para*-acids the solubility first increases and then decreases but in the case of the *meta*-acid, the solubility continuously decreases.

6. *The Influence of the Composition of the Acids.*—The composition of the acids too has got some significance in this effect. The order in which their solubilities are affected are almost the same but the degree of this effect varies. The stronger acids are influenced to a greater extent than the comparatively weaker ones. The acids with a nitro group in their composition are most influenced than the acids with an amino group and they in turn are more effected than the acids with hydroxyl group in their molecule.

As regards the mechanism of the phenomenon nothing can be definitely stated in absence of any conclusive evidence. Harkins, Brown and Davis (*J. Am. Chem. Soc.*, 1917, 39, 354) have tried to explain the solubility of various substances in water on considerations based on free energy decrease which is more or less a measure of the attraction of the active groups of the solute for the solvent molecules, and which to a secondary extent depends upon the shape and size of the molecules. According to them the solubility is a molecular scale phenomenon and is dependant upon the attraction of the different parts of the various molecules for each other and upon the shape and sizes of the molecules which must be fitted together to make a solution. However it is not very clear what would be the mechanism of the influence produced on the solubility of the acids by the addition of small quantities of electrolytes, and it is difficult to

understand how exactly the addition of the same quantity of the same electrolyte to the same acids having the same groups but different orientation should produce different effects. The authors think that it may probably be due to the formation of molecular complexes or some chemical interaction between acids and the electrolytes. Further experiments on viscosity, conductivity and absorption spectra are in progress in this laboratory.

We are thankful to Dr. S. S. Bhatnagar and Dr. Mata Prasad for their interest in the work.

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Investigations on the Acid Nature of some Derivatives of Sulphur, Selenium and Tellurium.

By
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Four principal methods were used by Hantzsch in supporting his extended theory of pseudo-acids. They have already been referred to in a previous paper (*this Journal*, 1925, 1, 247) and it has been shown that, according to the new theory, it was the "ionogen" bond between the "acid" hydrogen atom and the acid radical which was responsible for the acid properties and not the concentration of the hydrogen ion, as was supposed

in the classical electrolytic dissociation theory. The above methods (the comparison of the absorption spectra of the acid, its salts and esters in different solvents, the velocity of reaction of the acid with diazoacetic ester, the velocity of inversion of cane sugar in concentrated solutions and the action on indicators in different solvents) were then used to investigate acid properties of some derivatives of sulphur, selenium and tellurium, and conclusions drawn as to their comparative strength.

1. Methyl- and Ethyl-sulphuric Acids, RHSO_4 .

In pure condition these acids react very energetically with diazoacetic ester. Even very dilute aqueous solutions are active towards the indicator, and must therefore be classified as true acids corresponding to the formula, $[\text{RO}\cdot\text{SO}_3]\cdot\text{H}$. (In all these experiments dimethyl-amino-azobenzene was used as indicator). These acids, however, react as pseudo-acids in dilute alcoholic solutions, and even the concentrated ethereal solutions are neutral to the indicator. It must, therefore, be the pseudo-acid $\text{RO}\cdot\text{SO}_2\cdot\text{OH}$ which is present under these conditions.

2. Selenious Acid, H_2SeO_3 .

The conductivity of aqueous solutions of selenious acid has already been determined by Ostwald (Landolt-Börnstein, *Tabellen*, 1112). He came to the conclusion that this acid was one of the weak acids, for, even in a dilution of 1024 litres the conductivity was only about 60% of that of a monobasic acid. He therefore came to the conclusion that this acid was practically a monobasic acid of the formula $(\text{HO}\cdot\text{SeO})\cdot\text{H}$.

This acid was investigated according to all the four methods. The solid acid, provided it is absolutely dry, does not react with diazoacetic ester. The solution of the indicator in a solvent, which does not dissolve the acid,

is not colored red by the crystals of the acid. All these experiments lead us to the conclusion that the acid is a pseudo-acid of the formula $[(\text{HO})_2 \text{Se} \cdot \text{O}]_x$.

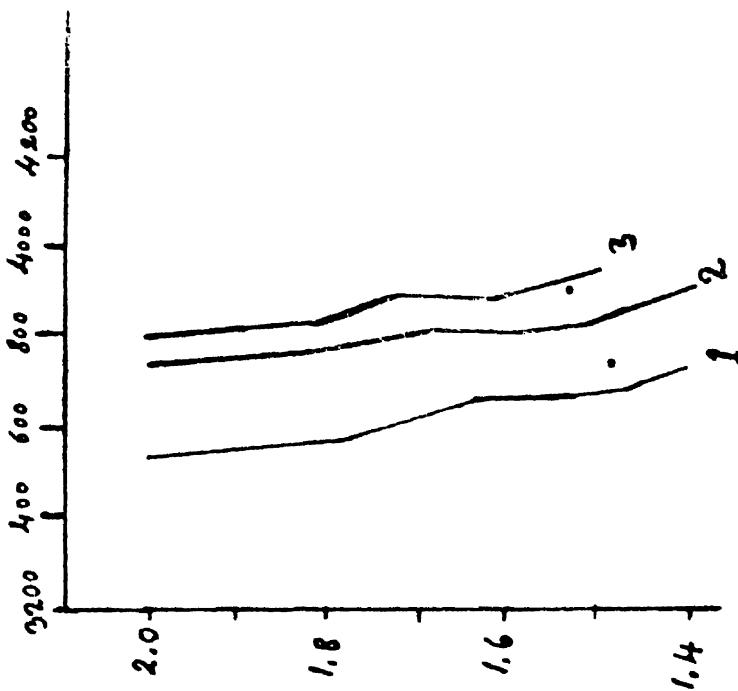
Table I gives the absorption spectrum of the acid in different solvents. Curve 1 corresponds to the absorption of a 0. 2*N* solution in aqueous alcohol, curve 2 to that of a similar solution in water, and also in 20% sulphuric acid (where the selenious acid is practically fully undissociated) and curve 3 to that of a solution of the acid in an excess of sodium hydroxide. The undissociated acid, the partially dissociated acid and the sodium salt show similar absorption. The alcoholic solution (which, according to the indicator experiments given below, contains only the pseudo-acid) has a slightly stronger absorption, and the order of succession of the curves is thus very similar to that of acetic acid (Hantzsch). We must, therefore, draw the conclusion that the molecules of the acid have been more or less saturated owing to the grouping of water molecules round them and have consequently a weaker absorption.

Table II gives the velocities of inversion of cane sugar by selenious acid in aqueous solutions. *x* Represents the amount of sugar inverted at the time *t* and *b*, the amount of sugar originally present in the solution. The constant *k* was then calculated according to the formula for monomolecular reactions :

$$k = \frac{1}{t} \log \frac{b}{b-x}$$

The equivalent activity (according to Ostwald, *J. pr. Chem.*, 29, 385) which is represented by *k/N* rises with increasing dilution, and indicates the increase in the concentration of the true acid in dilute solutions. The velocity of inversion *k* naturally decreases with increasing dilution. Table III gives a comparison of the values for

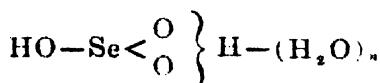
TABLE I.



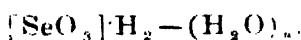
Absorption Spectra of Selenious Acid.

formic, acetic (A. Weissberger, *Dissertation*, Leipzig), and selenious acids. The order of magnitude of all the three acids is the same, and this is perhaps one more proof for the monobasic nature of selenious acid.

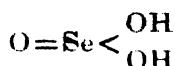
The velocities of reaction with diazoacetic ester are given in Table IV. The velocity is very small, and could not be determined in very concentrated solutions owing to the limited solubility of the acid in water. The aqueous solution can be completely neutralized in its action on diazoacetic ester by the addition of only one mol of alkali, and this proves that the true selenious acid present in the aqueous solutions is in the form of the hydrate of the monobasic acid :



and not as



The greater part of the acid is, however, present as the pseudo-acid,



or its hydrate.

With the addition of about 10 mols of alcohol the acid becomes completely inactive towards diazoacetic ester, and must therefore be present as the pseudo-acid in this concentration. The same solution is also neutral to indicators. The addition of a few drops of water produces however a sufficient amount of the true acid to give a red coloration.

The general conclusion to be drawn from all these experiments is that selenious acid is an associated pseudo-acid in the pure condition. The aqueous solutions contain a very large proportion of the pseudo-acid and only very small percentage of the hydrate of the true acid.

Even relatively concentrated solutions of the acid in alcohol contain only the pseudo-acid.

3. Selenic acid, H_2SeO_4 .

It was not possible to obtain the perfectly dry acid. The acid used in the experiments was 98%. It is known to be a strong acid, comparable in strength to sulphuric acid. It dissolves in water under considerable evolution of heat and forms the true hydroxonium salt $\text{HO} \cdot \text{SeO}_3 \cdot \text{H}_2\text{O}$. This aqueous solution therefore reacts very vigorously with diazoacetic ester, the reaction in a 0.3 N solution being very nearly explosive. A small amount of methyl alcohol was therefore added to this solution in order to transform some of the true acid into the pseudo-acid and thus reduce the velocity of the reaction a little. The reaction velocities are given in Table V. The values for sulphuric acid are also given for comparison.

The velocity increases more rapidly than the concentration, thus showing that the undissociated molecules of selenic acid are more active than the ions. The pure acid is therefore to be considered as the true acid, $[\text{SeO}_3\text{H}] \cdot \text{H}$ and the true oxonium salt as $[\text{SeO}_3\text{H}] \cdot \text{H}_2\text{O}$. This oxonium salt, as salt of a very strong acid and an exceedingly weak base ('water'), possesses "very nearly" but not exactly the same strength as the free acid. With increasing dilution, the amount of this salt increases and the velocity of the reaction decreases.

Like sulphuric acid (Hantzsch, *loc. cit.*) selenic acid exists as the true ethyl-oxonium salt even in the most dilute alcoholic solutions, and reacts energetically with diazoacetic ester, and also gives a coloration with the indicator. In other words, it dissolves in alcohol with the formation of the salt, $[\text{HSeO}_4]$, $[\text{H}_2\text{O}(\text{C}_2\text{H}_5)]$. Unlike sulphuric acid it does not dissolve appreciably in ether.

4. Sulphinic and Seleninic Acids, RSO_2H and RSeO_2H .

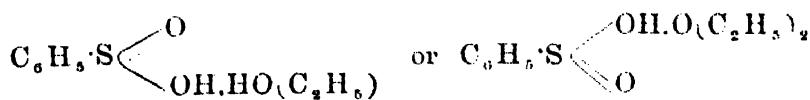
These acids are very difficult to obtain in the pure condition. It is well-known that the sulphonic acids are stronger than sulphuric acid. The reason of this is that the proportion of O : H is greater in the case of the former than in the case of the latter (3 : 1 as compared to 4 : 2). The "acid" hydrogen atom of the sulphinic acids can therefore be in loose connection with 3 oxygen atoms instead of with only 2 in the case of sulphuric acid. The sulphinic acids also fulfil the expectation that they would be stronger than sulphurous acid (O : H = 2 : 1 and 3 : 2).

(a) Benzenesulphinic Acid, $C_6H_5SO_2H$.

This acid is very unstable when exposed to the air. It decomposes diazoacetic ester only very slowly and the solid acid is therefore the pseudo-acid of the formula



In aqueous solutions the acid is present as the true acid, $C_6H_5-SO_2H$, as the solutions are active against both diazoacetic ester and the indicator. In about 50 mols. of alcohol it is completely transformed into the pseudo-acid, and ether inactivates it even in more concentrated solutions. In both cases we have the alcoholate or the etherate of the pseudo-acid,

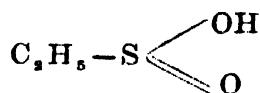


• in solution.

(b) Ethylsulphinic Acid, $C_2H_5SO_2H$.

This acid is a little weaker than the above, but still considerably stronger than sulphurous acid. 12.5 mols. of alcohol and 4.5 mols. of ether are necessary to make the acid completely inactive towards diazoacetic ester and the

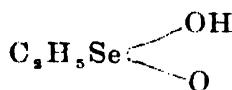
indicator. In these solutions, it is present as the pseudo-acid,



Both these acids are very unstable and have to be used up very soon after the preparation.

(c) Ethylseleninic Acid, $\text{C}_2\text{H}_5\text{SeO}_2\text{H}$.

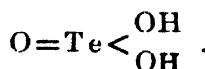
This acid could not be investigated in the pure condition, as it is even more unstable than the two acids mentioned above. The aqueous solution, prepared by addition of the calculated quantity of a strong acid to its salt, does not decompose diazoacetic ester. The change of color in the indicator caused by this solution is practically negligible and is completely destroyed by the addition of a couple of drops of alcohol. This acid is therefore present as the pseudo-acid,



even in aqueous solutions.

5. Tellurious Acid, H_2TeO_3 .

This acid is very weak and at the same time very sparingly soluble in water. It does not react with either diazoacetic ester or with the indicator. It is thus a pseudo-acid of the formula,



The salts of this acid can even be titrated by means of a strong acid just like carbonates or cyanides.

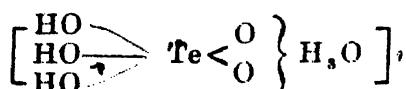
6. Telluric Acids.

It is known that telluric acid exists in three different modifications (*Mylius, Ber., 1901, 34, 2205*). The ordinary acid is a dihydrate $\text{H}_2\text{TeO}_4 + 2\text{H}_2\text{O}$, and is a very weak acid. The existence of a methyl ether of the formula $\text{Te}(\text{OCH}_3)_6$ indicates, however, that this acid could perhaps be better represented by the formula

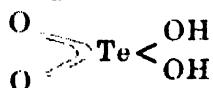
$\text{Te}(\text{OH})_6$. This acid when heated in a sealed tube to 140° is transformed into the so-called *allotelluric* acid which is obtained in the form of a sticky viscous mass and is a comparatively strong acid. The ordinary telluric acid possesses a normal molecular weight in water, while *allotelluric* acid has a molecular weight corresponding to a formula between $(\text{H}_6\text{TeO}_6)_3$ and $(\text{H}_6\text{TeO}_6)_4$. By heating both these acids in an open tube the pure acid, H_2TeO_4 , is obtained. The latter is insoluble in water and does not give an acid reaction.

All the three acids were investigated as regards their reactivity towards diazoacetic ester and the indicator. Ordinary telluric acid, which has a conductivity of the same order of magnitude as hydrocyanic acid, is inactive towards both these reagents and hence possesses the formula $\text{Te}(\text{OH})_6$. The potassium salt, obtained by precipitation with strong caustic potash, is very nearly completely dissociated in aqueous solutions, and the solution can be titrated against strong acids just like the corresponding carbonate or cyanide.

Allotelluric acid is a fairly strong acid and its aqueous solution has a high conductivity. It reacts vigorously with diazoacetic ester and the indicator. It can however be completely inactivated by the addition of about 4 to 5 mols. of alcohol (calculated on 1 atom of Te). *Allotelluric* acid must therefore be regarded as a true acid. Its behaviour and also its formation from the dihydrate can be best explained by means of the formula,



The pure acid is neutral towards both the above reagents and must be represented by the formula,



Hantzsch has already shown that the strength of an acid depends, in addition to the negative nature of the acid radical, on the ratio of the oxygen atoms of the acid radical to the acid hydrogen atoms. Sulphuric and selenic acids are thus strong acids and the latter is only slightly weaker owing to the less negative nature of its acid radical. It is also more easily transformed into the pseudo-acid. Ordinary telluric acid H_6TeO_6 has the ratio O : H = 6 : 6, and is naturally much weaker than both these acids. With increasing ratio of O : H the possibility of a hydrogen atom forming a hydroxyl group, characteristic of a pseudo-acid, naturally increases.

TABLE II.

*Velocity of Inversion of Cane Sugar with
Selenious Acid at 25.[°]*

10 % Sugar + 2N H_2SeO_3 ,				10 % Sugar + 0.5N H_2SeO_3			
Time (min.)	x	$\log b -$ $\log (b-x)$	k	Time (min.)	x	$\log b -$ $\log (b-x)$	k
0	0.0	0	0.0
50	1.5	0.391	0.000088	1365	2.51	0.687	0.000050
65	1.73	0.453	0.000080	2880	6.15	1.931	0.000067
245	2.6	0.701	0.000088	4560	8.87	3.161	0.000068
1315	4.1	1.163	0.000088	5700	10.15	3.893	0.000069
1700	5.3	1.574	0.000092	∞	17.45
2090	9.35	3.325	0.000083				
∞	17.45				
Mean value for k = 0.000086				Mean value for k = 0.000068			

$$\text{Equivalent activity} = \frac{k}{N} = \frac{0.000086}{2} = 0.000043 \text{ in } 2N \text{ solution}$$

$$\text{and } " = \frac{0.000068}{0.5} = 0.000136 \text{ in } 0.5N \text{ solution.}$$

TABLE III.

Velocities of Inversion of Cane Sugar with Formic, Acetic and Selenious Acids.

Formic Acid.			Acetic Acid.			Selenious Acid.	
Normality	k	$\frac{k}{N}$	•	k	$\frac{k}{N}$	k	$\frac{k}{N}$
4	0.000192	0.000048		0.000037	0.000009	—	—
2	0.0000978	0.0000489	—	—	—	0.000086	0.000043
1	0.000058	0.000058	—	—	—	—	—
0.5	0.0000332	0.0000664	0.0001	0.00002	0.0000683	0.00086	

TABLE IV.

Velocity of Reaction of Selenious Acid with Diazoacetic Ester.

Vol. of N_2 measured	0.01N	0.1N.
1.8 *	(0.00221)	(0.0294)
2.8	0.00284	0.0411
3.8	0.00301	0.048
4.8	0.00334	0.0516
5.8	0.00324	0.0533
6.8	—	0.0517
7.8	—	0.0444

* As exactly 1/1000 mols. of the acid and of diazoacetic ester were used, complete decomposition would have produced 22.4 cms. of N_2 measured at N. T. P. This volume, therefore, represented 8.8 of the reaction. The numbers in the first vertical column denote how much of the diazoacetic ester has been decomposed and the next two columns give the corresponding velocity constant at that time.

The bracketed values cannot be taken as certain, due to the disturbing influences at the beginning.

TABLE V.

*Velocities of Reaction of Selenic and Sulphuric Acids
with Diazoacetic Ester.*

Vol. of N ₂ measured. 8/8 = 22.4 c.cs.	0.005 N in water.	0.01 N in water.	0.1 N in water.	0.2 N in water.	0.3 N in 15% CH ₃ OH.	0.3 N in 30% CH ₃ OH.
Selenic Acid.	1/8	(0.0046)	(0.0089)	(0.134)	(0.296)	(0.74)
	2/8	0.0060	0.0106	0.196	0.490	1.15
	3/8	0.00625	0.0112	0.228	0.587	1.23
	4/8	0.00613	0.0106	0.240	0.675	1.19
	5/8	0.00540	0.0090	0.213	0.730	1.25
	6/8	—	--	0.210	0.645	1.17
	7/8	—	--	--	--	--
Sulphuric Acid.	1/8	0.00476	0.0081	(0.157)	(0.371)	0.955
	2/8	0.00593	0.00975	0.206	0.542	1.108
	3/8	0.00670	0.0099	0.248	0.711	1.175
	4/8	0.00647	0.0091	0.266	0.816	1.153
	5/8	—	0.0105	0.260	0.880	1.152
	6/8	—	--	0.217	0.768	1.110
	7/8	—	--	--	--	--

EXPERIMENTAL.

1. Selenious Acid.—Powdered metallic selenium was dissolved in concentrated nitric acid by warming and the solution heated to dryness. The residue was taken up with very little water and the acid purified by recrystallisation.

0.1292 g. selenious acid mixed with one drop of the indicator solution gave no coloration when 0.58 c.c. or 0.464 g. alcohol were added to it. In mols, this is equivalent to 10.1.

The velocity of inversion was measured by the usual method. The sugar solution was exactly 20% before being mixed with the acid solutions, which were 4*N* and 1*N* respectively. The strength of both the sugar and the acid were reduced to 10% and 2*N* and 0.5*N* respectively after mixing. The polarimeter tube was surrounded by a water-jacket through which a constant stream of water at 25° was kept running.

The velocity of the reaction with diazoacetic ester was measured according to the method described by Schreiter and Weissberger (*Dissertation*, Leipzig, 1924; see also this *Journal*, 1925, 1, 217). 0.1140 g. of the ester (0.001 mol) were always used. The vessels used in these experiments were carefully cleaned and in each case a few grains of pure sand, which had been previously boiled with acid and distilled water, were added in order to facilitate the evolution of the gas. The diazoacetic ester was first measured off by means of a calibrated pipette, a small known amount of water added and finally a slightly more concentrated solution of the acid than was required, thus producing the required concentration in the reaction mixture. The time and the volume of the nitrogen collected were then read off, the latter reduced to N.T.P. and the values for the coefficient were calculated according to the usual formula. The amount of diazoacetic ester taken would evolve 22.4 c.c. nitrogen after complete decomposition. The coefficients given in the Table in the theoretical part for $\frac{1}{8}$, $\frac{2}{8}$, etc., mean that the coefficient has been calculated for that particular time when the volume of nitrogen evolved was $22.4 \times \frac{1}{8}$, $22.4 \times \frac{2}{8}$, etc.

2. Selenic acid was prepared according to the method of Meyer and Moldenhauer (*Z. anorg. Chem.*, 1921, 116, 193). This consists of the oxidation of the selenious acid by means of chloric acid. The thick

syrup obtained in this way could not be completely dehydrated even after being kept for weeks in vacuum over P_2O_5 .

3. Methyl and ethyl sulphuric acids could not be prepared by Kremann's method (*Monatsh.*, 1900, 31, 216) as this was both costly and troublesome. The method of Berthelot (*Bull. Soc. Chim.*, [2], 19, 295) gave quite satisfactory yields. The only precaution, that is absolutely necessary, is the concentrating of the solution of barium ethyl sulphate in vacuum at a temperature not exceeding 55° .

4. Tellurious acid was prepared in exactly the same manner as the corresponding selenium compound. The acid is insoluble in water but soluble in alkalis.

5. Telluric acid was prepared by the method of Mylius (*loc. cit.*), by the oxidation of the lower acid by means of chromic acid. *Allotelluric* acid was prepared by heating the ordinary acid for 3 hours in a sealed tube at 140° . It has a slightly yellow color when hot but is colorless when cold.

6. Benzenesulphinic Acid.—20 g. Benzenesulphonyl chloride were dissolved in water and 10 g. of zinc dust were added slowly under cooling. The mixture was cautiously poured into water and filtered. The insoluble part containing the zinc salt and the unused zinc dust was then suspended in water and soda solution added to it. The filtrate from this mixture contained the sodium salt which was purified by crystallisation, decomposed by means of the calculated quantity of hydrochloric acid and the acid thus obtained was washed and dried. White needles, m. p. $83-84^\circ$. For inactivation against the indicator, 0·284 g. required 6·2 c.c. or 4·96 g. alcohol. This corresponds to 53·5 mols.

7. Ethylsulphinic acid was prepared by means of Grignard's reaction. 20 g. of ethyl bromide were

dissolved in 50 c.c. of dry ether and 4.2 g. magnesium ribbon were added in small pieces. After the reaction was finished a stream of dry SO_2 was passed into it and the flask strongly cooled. The white precipitate of the magnesium salt was thoroughly washed and dried. It crystallises with 2 molecules of water. The salt was then decomposed by the calculated amount of dilute sulphuric acid. It is obtained in the form of a colorless syrup and decomposes slowly at the ordinary temperature. 2.1 g. Mg salt + 0.98 g. sulphuric acid (calculated amount) + 1 drop of the indicator required 14.4 c.c. or 11.52 g. alcohol and 9.25 c.c. or 6.66 g. ether for complete inactivation. This corresponds to 12.5 and 4.3 mols. respectively.

8. Ethylseleninic acid was prepared in exactly the same manner as above, using selenium dioxide instead of sulphur dioxide. This acid has practically no acidic properties and even forms a compound with hydrochloric acid having the formula $\text{C}_2\text{H}_5\text{SeO.OH.HCl}$ (Rathke, *Ann. Chem.*, 1869, 152, 216).

In conclusion I wish to thank Geh. Rat. Prof. Dr. A. Hantzsch for the kind interest he has taken in the progress of the work.

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Dehydrogenation of Methyl Alcohol and Formaldehyde with Copper as Catalyst. A Study of the Conditions of the Equilibrium in the System : $\text{HCHO} \rightleftharpoons \text{CO} + \text{H}_2$,

BY

JNANENDRA CHANDRA GHOSH

AND

JOGENDRA NATH CHAKRAVARTY.

In a paper by Ghosh and Mali (this *Journal*, 1924, 1, 37) on the vapour pressure and chemical constant of formaldehyde it was suggested that the determination of chemical constant of this gas would be helpful in studying the conditions of equilibrium in the following reactions.



Sabatier and Mailhe found that with freshly reduced copper oxide at temperatures between 200° and 300° , "the thermal decomposition of methyl alcohol proceeds according to the equation (1) and the reaction is a reversible one. A 50% conversion is obtained with a 5% loss of decomposition products and 45% unchanged methyl alcohol" (Rideal and Taylor, *Catalysis in Theory and Practice*, p. 127).

That the decomposition of HCHO into CO and H_2 is a reversible one is suggested by Badische Patent

(Brit. Pat. 20486, 1913) and Dreyfus Patent (D.R.P. 108855, 1915) according to which formaldehyde is obtained by passing a mixture of carbon monoxide and hydrogen in the ratio of 2 to 1 at 100 atmospheres over catalytic materials at 300°–400°. Some unpublished investigations of Mr. K. P. Bose in this laboratory showed that equilibrium in the above reactions could not be attained by passing methyl alcohol vapour slowly over a space packed up with the catalyst below 300° as shown from the analysis of the outflow gases. The yield of formaldehyde and its decomposition into CO and H₂ was found to depend more on the nature of the catalyst than on the velocity of flow at a particular temperature. Thus with copper catalyst, obtained by reduction of freshly precipitated copper hydroxide, dehydrogenation of methyl alcohol began at 110° and at 170° it was about 40 per cent. Orange-red compact copper prepared by reduction of the dense oxide according to Sabatier's method gave only 10% yield of formaldehyde at 20°. Hence in these investigations a static method of attaining gaseous equilibrium was adopted. The arrangement was in many respects analogous to that devised by Rideal for measuring the hydrogenation of ethyl alcohol and acetone (*Proc. Roy. Soc., [A] 99, 155*).

EXPERIMENTAL.

The experimental arrangements will be clear from the diagram (Fig. 1). An electric tube-furnace, F, was maintained at a constant temperature for 10 to 15 hours at a stretch from a constant current battery of 220 volts. The range of temperature lay between 155° to 350°. The bulb of the reaction tube, T, was at the centre of the furnace and at the same temperature throughout its entire length. The tubes had capacities varying from

40—70 c.c. and were attached to a capillary tube with a side tube at one end which communicated through the stop-cock, *S*, with a mercury manometer, *M*. The bulb was filled with small pieces of pumice stone which were soaked with copper formate solution and ignited at 300° in a current of air (for details see Palmer, *Proc. Roy. Soc.*, [A], 98, 13). The open end of the reaction tube was then drawn into a capillary, care being always taken that the length of the bulb of the reaction tube did not exceed two-thirds of the length of the furnace. The catalyst material was then reduced *in situ* by passing a current of pure hydrogen for six hours at a temperature of 250°. The stop-cock *S* was closed, methyl alcohol vapour from a twice distilled sample was passed into the reaction tube, the hydrogen inside was chased out and the ends sealed at constrictions previously made, first at *C*, then at *C'*. The furnace was maintained at the desired temperature and the pressure inside the tube at constant volume was noted by bringing the mercury level to a certain mark, *m*, above the stop-cock. The ends of the reaction tube projecting out of the furnace were wound round with manganin wire and maintained at about 100° by electrical heating. The vapours of alcohol were thus prevented from condensing in the capillary ends. The reaction was allowed to go on for twelve hours to ensure complete equilibrium which was indicated by constant pressure in the manometer. The capillary end *C* was then connected with rubber tubing to a carbon dioxide generator and *C'* to a Hempel gas burette. The capillary ends were broken inside the rubber tubing by applying pressure and the vapours inside the reaction tube were quickly chased out by carbon dioxide and collected over caustic soda solution in the gas burette. It is of course assumed that during the process of the collection of the gases the condition of the equilibrium

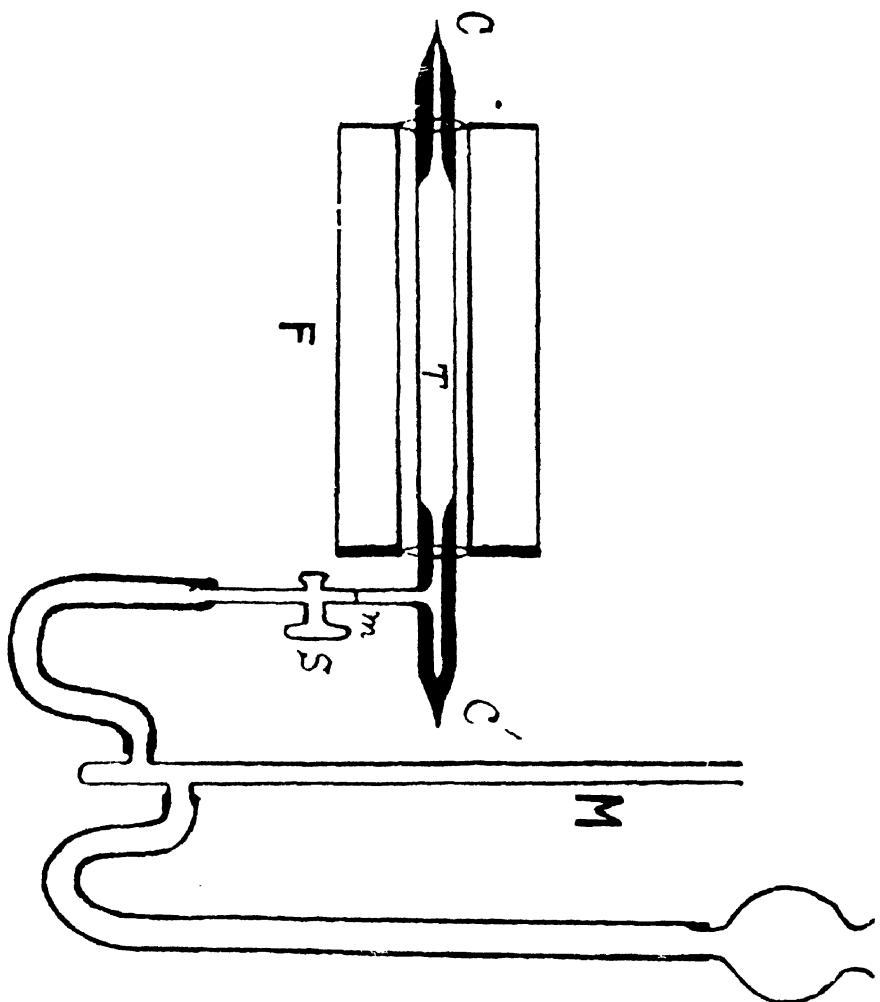


FIG. 1.

is not disturbed. The gas mixture contained hydrogen, methane and carbon monoxide and was analysed in the usual way. The aqueous solution was analysed for methyl alcohol and formaldehyde. The latter was estimated by Romijn's method. The total amount of formaldehyde and methyl alcohol was estimated by complete oxidation with $2N$ chromic acid and sulphuric acid and titrating back the chromic acid with potassium iodide solution (*Ber.*, 39, 325). Formaldehyde could also be indirectly estimated, for, it will be equivalent to the volume of hydrogen minus twice the volume of carbon monoxide in the mixture. Above 290° the formation of methane becomes appreciable and then it is not possible to determine the exact quantity of formaldehyde by the indirect method. We might assume, however, that at these temperatures, methane is formed according to the Armstrong-Hilditch reaction (*Proc. Roy. Soc.*, 103, 25),

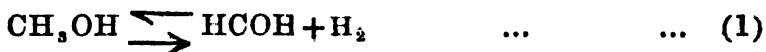


and the amount of formaldehyde could thus be indirectly estimated. The amount of CO_2 in the gas mixture under equilibrium conditions could not be directly estimated but it could be estimated as equivalent to the amount of methane present. In fact the previous investigation of Bose showed that at these temperatures CO_2 and CH_4 were formed in equivalent quantities. The quantities of each of the following substances, *viz.*, CO , H_2 , CH_4 , CO_2 , HCHO and CH_3OH being known it is possible to calculate the partial pressure of each from the observed total pressure. It is obvious that the apparatus has to be dismantled after each experiment, and the catalyst has to be prepared anew. This is necessary in view of the well-known fact that the activity of the catalyst rapidly diminishes with time.

The values of equilibrium constants at 340° and 330° were not very reliable as the quantities of formaldehyde were small for direct estimation and the indirect estimation becomes somewhat uncertain because of the increasing quantities of methane being formed at higher temperatures. Beyond 345° the equilibrium could not be determined.

Experimental Results and Discussions.

Tables I and II give respectively the observed equilibrium constants of the reactions (1) and (2).



$$K_p(1) = \frac{p_{\text{HCHO}} \times p_{\text{H}_2}}{p_{\text{CH}_3\text{OH}}} \quad \text{and} \quad K_p(2) = \frac{p_{\text{CO}} \times p_{\text{H}_2}}{p_{\text{HCHO}}}$$

TABLE I.

T	K _p (obs.)	K _p (cal.)
155°C	.37	.39
205°C	.65	2.24

K_p (cal.) in column 3 of the Table I is obtained from the equation,

$$\log_{10} K_p = \frac{-10700}{4.571T} + 1.75 \log_{10} T - 3.75 \times 10^{-4} T + .8 \quad \dots \quad (i)$$

Rideal gives the following theoretical equation for the decomposition of ethyl alcohol,

$$\log_{10} K_p = \frac{-10700}{4.571T} + 1.75 \log_{10} T - 3.75 \times 10^{-4} T + 2.2$$

The heat of dissociation of methyl alcohol into formaldehyde and hydrogen cannot be fixed with certainty as the exact heat of formation of formaldehyde is not known. Rideal gives 10700 cals. as heat of dissociation of ethyl alcohol. The heat of dissociation of propyl alcohol is 10450 cals. (heat of formation of propyl alcohol being 65690 cals. and that of propionic aldehyde 55240 cals. Thomsen, *Thermo-Chemistry*). We are therefore, not very much wrong in fixing the heat of dissociation of methyl alcohol at the above figure. The chemical constant of hydrogen according to Nernst is 1.6. But Bakhuyzen in a recent paper (*Z. physikal. Chem.*, 1924, 111, 57) from a critical examination of the available data gives the value of the chemical constant as 1.1. For formaldehyde $C = 3.5$, for methyl alcohol C might be taken to be 3.8, the same as propyl alcohol. Therefore $\Sigma vC = 0.8$. The agreement between observed and calculated values of K_p at 155° is accidental. It is obvious that at 205° the dissociation of methyl alcohol corresponding to the conditions of equilibrium is not obtained. If, however, we take the chemical constant of methyl alcohol as 4.1 the same as that of ethyl alcohol, then $\Sigma vC = 0.5$ and the calculated values of K_p at 155° and 200° are 0.195 and 1.12 respectively. The agreement with the observed values is no better.

TABLE II.

T°C.	155°	160°	205°	230°	250°	260°	295°	330°	340°
K_p (obs.)	0.032	0.036	0.13	0.27	0.48	0.56	0.94	1.6	2.20
K_p (cal.)	0.028	0.032	0.13	0.32	0.40	0.50	0.98	1.9	2.21

K_p (cal.) in Table II is obtained from the equation,

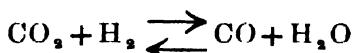
$$\log_{10} K_p = \frac{-11800}{4.571T} + 1.75 \log_{10} T - 0.001T + 0.3 \quad \dots \quad (ii)$$

The agreement is fairly good throughout. The difference between the heats of combustion of methyl alcohol and of carbon monoxide and $2H_2$ is 22550 calories. If the heat of dissociation of methyl alcohol into formaldehyde and hydrogen is fixed as 10700 cals. the heat of dissociation of formaldehyde into carbon monoxide and hydrogen comes out to be 11800 cals.

The Chemical Constant of Carbon Monoxide.

Nernst gives 3.5 as the chemical constant of carbon monoxide. Jellinek (*Physikalische Chemie der Gas Reaktionen*, p. 466) gives 2.6 as the chemical constant of carbon monoxide. The chemical constant of nitrogen is 2.6 and in view of the fact that the physical properties of carbon monoxide and nitrogen are very similar as has been emphasised by Lewis and Langmuir, it appears that the value 2.6 for carbon monoxide is the probable one. Further according to Nernst the chemical constant of a gas is given by the empirical equation, $C = 0.14 \frac{\lambda}{T_b}$, where λ = molecular latent heat of vaporisation, T_b = boiling point in absolute temp. at one atmosphere. From Landolt and Börnstein's *Tables*, 1923, we get $\lambda = 1414$ cal. and $T = -190^\circ$, whence $C = 2.4$.

The water gas reaction,



has also been very thoroughly investigated by Hahn (*Z. physical. Chem.*, 44, 513) and Engels (*Z. f. Gas Beleuchtung*, 62, 483) whose results are in mutual agreement. Sackur has shown that for this reaction the equation,

$$\log K_p = -\frac{2200}{T} + 2.0$$

gives values in agreement with the experimental data (*Thermo-Chemistry and Thermo-Dynamics*, Eng. Trans.,

1917, p. 314). ΣvC for the above reaction is therefore 2·0. C for hydrogen is 1·1; for water 3·6; for carbon dioxide 3·2 (Nernst's data) and C for carbon monoxide is 2·7. It thus appears that 2·7 is the more probable value for carbon monoxide and ΣvC in the reaction,



is therefore equal to 0·3. This is the value that has been taken in equation (ii).

It is thus clear from this investigation that the equilibrium conditions for dehydrogenation of methyl alcohol cannot be exactly ascertained with copper prepared in the usual way as the catalyst. But the dehydrogenation of formaldehyde appears to be a reversible reaction and the variation of equilibrium constants with temperature can be fairly well expressed by an equation of the Nernst type.

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Catalytic Formation of Methane from Carbon Monoxide and Hydrogen.

Part I.

BY

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Production of methane from carbon monoxide is a very important technical process, and in the Cedford process a mixture of hydrogen and carbon monoxide in the ratio of 5 to 1 volumes is passed over nickel catalyst at about 300°C resulting in the complete conversion of carbon monoxide into methane. Theoretically three volumes of hydrogen are required for one of carbon monoxide but in actual practice it is found that if the percentage of carbon monoxide in the mixture is kept above 17%, the catalyst is quickly spoilt by carbon deposition due probably to the reaction,



The attainment of the hydrogen-rich gas by partial removal of carbon monoxide from blue water-gas by liquefaction is an operation of considerable expense and the Cedford process is not a commercial success.

Medsforth has recently studied (*J. Chem. Soc.*, 1923, 123, 1452) the action of various promoters on the velocity of methane formation by nickel catalyst in a gas mixture of carbon monoxide and hydrogen (1 : 5) and finds that the efficiency of the promoters runs parallel with their catalytic dehydrating capacity. He suggests the following mechanism for the reaction :



According to him cerium oxide is the best promoter for this reaction.

In our experiments the chief object was to prepare a catalyst which would retain its activity undiminished in a gas mixture of H₂ and CO in the theoretical ratio of 3 : 1. It was felt that if the poisoning of the catalyst is due to carbon deposition on nickel surface, a nickel surface deposited on carbon itself would have better chance of retaining its activity, for the atoms of carbon produced in reaction (1) might get fixed to particles of carbon which form the support of the nickel catalyst in preference to the atoms of nickel. This expectation was realised in actual experiment and it was found that a sugar-charcoal-nickel catalyst retained its activity for months.

EXPERIMENTAL.

A mixture of concentrated cane-sugar solution and Kahlbaum's nickel acetate was dropped into a strongly heated nickel crucible with a very smooth surface from a separating funnel; the quantity of solution dropped each time should on no account exceed the amount which could swell up and partially carbonise instantaneously. When a considerable quantity of this voluminous and partially carbonised product was obtained, the crucible was heated from all sides, until the catalyst just began to burn of itself. The crucible was then covered with lid and the product further heated from below until the evolution of fumes ceased. The product obtained was finally heated strongly in an asbestos-covered hard glass tube, in absence of air till all gases ceased to come out. To get voluminous active product too much of sugar must be avoided and the surface of the nickel crucible must be very smooth. Before use the catalyst was reduced in a current of purified hydrogen for twenty-four hours at temperatures between 210° and 250°. Carbon monoxide and hydrogen were prepared by the action of sulphuric acid on sodium formate and zinc

respectively, purified in the usual way and stored in a large glass vessel in the ratio of 1 : 3 volumes. The gas mixture was passed over the catalyst at various speeds by forcing water under pressure in the storage vessel and was desiccated on its way. The catalyst material was at the centre of a hard glass tube with asbestos plugs on either sides, and was heated uniformly in an electric tube furnace, which was maintained at any constant temperature by regulating the current. The outflow gases were collected from time to time in a Hempel gas burette and analysed in the usual way. The rate of passing of gas was measured by means of a flow-meter. The temperature could be seen from a mercury thermometer placed in contact with the catalyst material. The experimental data are given in Tables I and II, where *S. V.* = space velocity, i.e., c.cs. of gas per c.c. of catalyst material per minute.

TABLE I.

Catalyst :—Sugar-Charcoal-Nickel (73 : 27). Composition of Outflow Gases.

T° C	S.V.	% CH ₄	% CO ₂	% CO	% H ₂
300	0.33	75	9	0	16
	0.74	62	9.8	0	28
	1.03	53	8.8	0	38
	2.40	33	6.1	9.7	51.3
335	1.55	68	9.4	0	22.5
	1.76	65	9.5	0.7	24.7
358-360	1.69	65.7	7	0	27.4
	3.54	54.0	9.5	0	36.0
	3.60	50.0	10.5	0.6	39.0
405	4.32	63	9	0	28

TABLE II.

Catalyst: Sugar-charcoal-Nickel-Ceria¹

T°C	S.V.	% CH ₄	% CO ₂	% CO	% H ₂
300	2·6	30	4·2	12·3	54
355	2·1	67·5	8·4	0	23·6
	3·4	65·4	8·9	0	25·3
	4·4	57·4	8·4	0	34

It was noticed that traces of nickel got deposited on the sides of the tube on allowing the sugar charcoal catalyst to cool in an atmosphere of the reaction mixture from a temperature of 500°. But in the case of ceria as a promoter of the catalyst, such a deposit appeared on cooling from 300°. This phenomenon did not occur when the catalyst was cooled in a current of hydrogen.

It will be noticed from Table I that for every temperature there is a critical space velocity beyond which CO appeared in the outflow gases. This critical velocity increases considerably as the temperature of the reaction increases. Thus at 300° this critical space velocity is about 1·3, at 335° it is 1·7, at 358°, 3·6 and at 400° it lies above 4·3. With ceria as promoter the efficiency of the catalyst increases but not to the extent found by Medsforth with nickel catalyst supported on pumice stone. Thus at about 355°, the critical space velocity is 3·5 without ceria, while with ceria it is above 4·4.

Origin of CO₂ in the Outflow Gases.

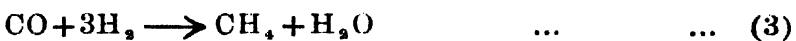
The experimental data recorded above disclose the drawback that with this particular catalyst a considerable

¹ Sugarcharcoal : Nickel : Cerium nitrate
80 27 23

amount of CO_2 is produced. Carbon dioxide may be produced by either or both of the following reactions :—



The analysis of the incoming and the outflow gases makes it possible to decide which of these reactions is responsible for the production of CO_2 . If 75 vols. of hydrogen and 25 vols. of carbon monoxide give x vols. of CH_4 and y vols. of CO_2 and z vols. of hydrogen then, if reaction (1) alone were to proceed, besides methane formation according to reaction,



the relative volume of $\text{CH}_4 : \text{CO}_2 : \text{H}_2$ would be $(25-2y) : y : 75-3(25-2y)$ or $(25-2y) : y : 6y$ (Eq. 1). Whereas if reaction (2) were to proceed only, the relative volumes of $\text{CH}_4 : \text{CO}_2 : \text{H}_2$ would be as $(25-2y+y) : y : 25-y$ or as $25-y : y : 75-3(25-2y)-2y$ or as $25-y : y : 4y$. (Eq. 2)

In the previous tables it will be seen that the ratio of CO_2 to H_2 is never as $1 : 6$ indicating that reaction (1) is not taking place at all. The ratio is in some cases approximately $1 : 4$. The formation of CO_2 is purely due to reaction (2). In the majority of cases part of the carbon dioxide is produced by reaction (2) but a considerable portion must be produced by some other type of reaction. Perhaps here we are dealing with the reaction,



with water vapour produced in reaction (3). If this reaction were only to proceed then



From the tables it is at once apparent that reaction (4) alone is not responsible for the production of CO_2 except in the case recorded in Table I for 300° with space velocity of 0.33. In fact in the majority of cases it

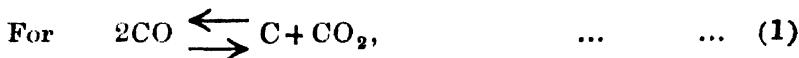
is produced partly by reaction (2) and by (4). If y of CO_2 is made of y_2 and y_4 , or if $y = y_2 + y_4$ then

$$x : y : z :: (25 - 2y_2) : y_2 + y_4 : [75 - 3(25 - 2y_2) - 2y_2 + 2y_4]$$

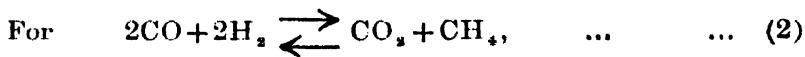
$$\text{or } 4y_2 + 2y_4$$

The ratio $x : y : z$ being known y_2 and y_4 can be calculated. Calculations according to Eq. 4 show that as the space velocity increases, reaction (4) tends to be suppressed until for high space velocities reaction (2) alone becomes responsible for the production of CO_2 .

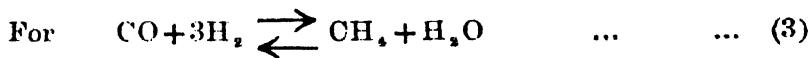
The equations showing the variation of equilibrium constants with temperature for reactions involved here are given below.



$$\log K_p = \frac{37,600}{4.571T} - 1.75 \log T + 0.006T - 3.8$$

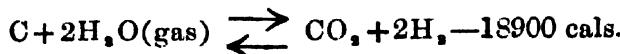


$$\log K_p = \frac{57,250}{4.571T} - 3.5 \log T - 4.5$$

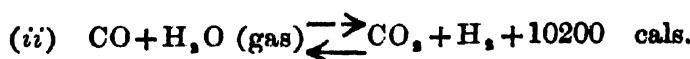
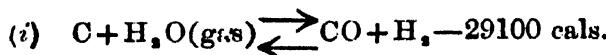


$$\log K_p = \frac{47,150}{4.571T} - 3.5 \log T - 2.2$$

and for the reaction (4)



which might be split up into reactions,



and the approximate Nernst equation will be

$$\log K_p = -\frac{18,900}{4.571T} + 1.75 \log T - 8$$

It will be noticed that as the temperature increases the formation of carbon dioxide, according to equation (4), is favoured and the quantity of CO in equilibrium with CH₄, according to Eqs. 2 and 3 ceases to be negligible.

Summary.

(1) A sugar-charcoal-nickel catalyst for the reaction, $\text{CO} + 3\text{H}_2 = \text{CH}_4 + \text{H}_2\text{O}$ retains its activity undiminished for months when the ratio of H₂:CO is 3:1 and the critical space velocity below which CO disappears from the outflow gases is quite large.

(2) This catalyst entirely suppresses the reaction $2\text{CO} = \text{C} + \text{CO}_2$ and prevents the deposition of carbon on nickel surface.

(3) Ceria acts as a promoter for this catalyst.

(4) Some amount of CO₂ is generated during the operation which is mainly due to the reaction, $2\text{CO} + 2\text{H}_2 = \text{CO}_2 + \text{CH}_4$ and partly to the reaction, $\text{C} + 2\text{H}_2\text{O} = \text{CO}_2 + 2\text{H}_2$

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Catalytic Formation of Methane from Carbon Monoxide and Hydrogen.

Part II.

Production of Fuel Gases rich in Methane

BY

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AND

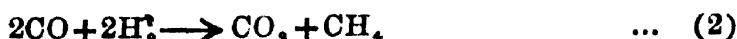
JNANENDRA CHANDRA GHOSH

Blue water gas and carburetted water gas have the following approximate composition :—

	H ₂	CO	CO ₂	CH ₄	N ₂	Unsaturated hydrocarbon.
Blue water gas	49	42	4	5	4.5	
Carburetted water gas	38	27	3	17	5	10

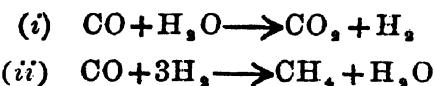
Owing to the poisonous properties of blue water gas with its high carbon monoxide content it is not used for distribution in a city supply; "the chief application of blue water gas is in connection with the manufacture of carburetted water gas," which "is even used for distribution without admixture in the United States." (Greenwood, *Industrial Gases*, pp. 324-325.)

It has been noted in the previous paper that sugar-charcoal-nickel catalyst remains active for months in a gas mixture H₂ : CO :: 3 : 1 and always produced a certain amount of CO₂ and CH₄ according to the reaction,



This led to the hope that this catalyst might be used for converting blue water gas into carburetted water gas. Armstrong and Hilditch observed (*Proc. Roy. Soc.*, 1923, [A], 103, 27) that when a mixture of carbon monoxide

and hydrogen was passed over nickel catalyst, the above was the only reaction taking place 'towards $300^{\circ}\text{C}^{\circ}$ '. Unfortunately Armstrong and Hilditch have not described their method of preparing this catalyst and only mention that nickel was deposited on kieselguhr. They advance the view that the reaction takes place in two stages :



The nickel of the catalyst studied in this paper was deposited on pumice stone, sometimes along with sugar charcoal and the effects of various promoters on these catalysts have also been investigated.

EXPERIMENTAL.

Preparation of Nickel Catalyst with Sugar Charcoal and Pumice powder as supporting Material with or without Promoter.—A solution of weighed quantities of sugar, nickel acetate and promoter, if any, was prepared and concentrated carefully so as to give on addition of pumice powder a semi-solid mass. Merck's ignited pumice stone was broken to small pieces, kept for three days in nitric acid, washed and ignited before use. This product was mixed with a small quantity of powdered ammonium carbonate and heated in a smooth nickel crucible with the lid on to dull redness. When the product swelled up the lid was opened and stronger heating applied till the carbon in the catalyst began to burn by itself. With very fine pumice powder the catalyst was neither very voluminous nor very active. Other experimental details were the same as in the previous paper excepting that the reacting gas mixture had the composition $\text{H}_2 : \text{CO} :: 1 : 1$.

Table I gives a comparative idea of the efficiency of the catalyst for $1 : 3$ and $1 : 1$ mixture of CO and H_2 .

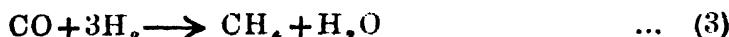
TABLE I.

Catalyst	Pumice	:	Nickel acetate	:	Sugar.
	17		4·7		16.
Quantity of nickel per c.c. of catalyst		0·018 gm.
Temperature of reduction		265°

S.V. = c.c. of gas per c.c. of catalyst space per minute.

H ₂ : CO	Temp.	S. V.	% CH ₄	% CO ₂	% CO	% H ₂
3 : 1	300°	1·22	50	12·5	0	37·7
	"	1·63	40·2	10·3	2·3	46·8
	356°	1·52	54·2	10·8	0	35·1
1 : 1	310°	0·38	18·5	9·6	43·6	28·1
	355°	0·59	28·4	19·9	29·1	24·5 *
	385°	0·34	36·0	34·0	11·9	18 *

From Table I it is clear that the efficiency of the catalyst for reaction (2) is small and an attempt was made to improve the efficiency by various promoters. Ceria as promoter, found by Medsforth (*J. Chem. Soc.*, 1923, 123, 1452) to be most efficient for the reaction,



is without much influence on pumice-nickel-sugar catalyst in promoting reaction (2) as will be evident from Table II.

TABLE II.

Catalyst	Pumice	:	Nickel acetate	:	Sugar	:	Cerium Nitrate.
	17		3·5		11·3		0·258
Quantity of nickel per c.c. of catalyst					0·0155 gm.
Temp. of reduction		265°

Temp.	S. V.	% CH ₄	% CO ₂	% CO	% H ₂
350°	·4	28·7	21·3	27·3	22·4 *
350°	2·6	10	4·7	48	37·2.

* See footnote, p. 161.

Vanadic acid was found by Medsforth to be the least efficient promoter for reaction (3). It was considered interesting to investigate its efficiency for reaction (2).

TABLE III.

Catalyst	Pumice	:	Nickel acetate	
	3		1	
Quantity of nickel per c.c. catalyst			... 0·037 gm.	
Temp. of reduction	...		280°	
Temp.	S.V.	% CH ₄	% CO ₂	% CO
309°	·63	37	31·9	12·6
				% H ₂
				18·5*
Catalyst	Pumice	:	Nickel acetate	: Vanadic acid
	17		3·5	0·3
Nickel per c.c. of catalyst				0·225 gm.
Temp. reduction				286°
Temp.	S. V.	% CH ₄	% CO ₂	% CO
(1) 304°	·68	51·9	43·2	3
				1·8 *
Followed by a rapid fall in activity.				
A day after (1). "				
(2) 302°	0·42	29	22	31
Five days after (2).				
(3) 305°	0·44	21	9	47
After two days' working at temperature between 460° and 524°.				23
(4) 304°	0·49	14	4·8	50
				31

It will be seen from Table III that vanadic acid is a very efficient promoter on nickel catalyst for reaction (2). But unfortunately the activity does not remain constant as will be evident from the data given. After 9 days' work the CO₂ formation at 304° drops from 43% to 5%. †

It was observed that a considerable deposit of nickel formed on the sides of the tube and a deposit of carbon on the pumice stone. Deposition of nickel was also observed when the catalyst was worked even below 305°. The fall of activity was also noticed when the catalyst

* The excess of hydrogen in the initial readings is mainly due to hydrogen already present in the reaction tube.

† After each day's experiment the catalyst was allowed to cool in an atmosphere of H₂ and CO mixture (1: 1) for about 18 hours. The catalyst was worked almost continuously for 6 hours every day.

was cooled in an atmosphere of pure H₂ during intervals between successive days' work. But here the deposition of nickel could not be observed.

It will be noticed from the analytical data at 300° to 305° that with continued use, the difference between the percentage yields of CH₄ and CO₂ increases continuously. This is ascribed to the fact that reaction (3) is taking place in larger portion.

An attempt was made to find out if by the use of sugar charcoal the high efficiency observed in the catalyst, pumice-nickel-vanadic-acid, can be maintained steady. The results are summarised in Table IV.

TABLE IV.

Catalyst	Pumice powder : 17	Nickel acetate : 3·5	Vanadic Acid : 0·25	Sugar. 10
Quantity of nickel per c.c. of catalyst	...	0·0157 gm.		
Temp. of reduction	...	279°		

Temp.	S. V.	CH ₄	CO ₂	CO	H ₂	Diff.
300°	... 54	19·2	11·1	42·7	27	0·5
351°	... 1·95	26	25·4	25·3	23·2	-0·9
"	... 2·7	24·5	20·4	32	23·4	-0·6
353°	... 4·7	14	6	48	32	0
406° [A]	... 5·7	34·2	33·5	14·6	17	3·8*
405° [B]	... 10·8	25·3	24	26·2	24	2·6*
451° [C]	... 25·4	20	16	36	27·6	-0·4
506°	... 36·9	18·1	14·2	37·2	30·8	1 *
540°	... 41·9	19·4	17·4	32·5	30·5	2 *
600°	... 45·5	8·5	5·5	46·3	39·6	-0·6

* It was invariably found that as the temp. of the catalyst was raised the analysis of the outflow gases for the first few minutes showed an excess of hydrogen. This was due to the fact that a large amount of hydrogen was absorbed by nickel-charcoal surface part of which was given out when the temperature was made higher.

A large number of experiments were carried out with this catalyst for months and the data recorded in Table IV are only typical. The significant fact to be noted in connection with this catalyst is that its activity is rather low at low temperature; but as temp. rises the activity rapidly increases. The activity remains steady for months if the reaction temp. is not maintained above 500°. Continued reaction at 500° for some time completely spoils the catalyst. When not in use the catalyst was kept in an atmosphere of hydrogen. It was noticed generally that with increase in *S. V.* at constant temperature the difference between the percentage yield of methane and carbon dioxide increased indicating that high *S. V.* favours reaction (3). The same phenomenon was observed in Table IV, where temperature and *S. V.* were kept practically constant but activity of the catalyst was diminishing. Both the reactions (2) and (3) take place with evolution of heat and it was found that at about 400° the reaction proceeded quickly enough to maintain constant the temperature of the catalyst-space without extraneous heating.

Pumice and sugar charcoal were in some experiments replaced by cocoanut charcoal. The initial activity was found to be quite high at low temperature but unfortunately the activity did not remain steady. It also did not increase much with increase of reaction temperature. Besides vanadium pentoxide, ferric oxide was found to be a suitable promoter. Table V gives the experimental data.

TABLE V:

Catalyst	Pumice : 17	Nickel acetate : 3·5	Ferric nitrate : 0·8	Sugar 17
Nickel per c.c. of catalyst		0·01 gm.
Temp. of reduction		260°
Temp.	S. V. 305°	CH ₄ 19·6	CO ₂ 8	CO 48·8
	·78			H ₂ 23·8

It will be noticed that with this catalyst the difference between the percentage of CH_4 and CO_2 is very large, more than 50% of CH_4 yield being due to reaction (3).

Table VI gives the approximate calorific value per 22.4 litres.

TABLE VI.

	CH_4	CO_2	CO	H ₂	N ₂	Unsaturated hydrocarbon	Calorific value
Carburetted water gas	17	3	27	38	5	10	100,000
Methane-rich gas							
<i>vide Table IV</i> [A]	34.2	33.5	14.6	17	94,000
"	25.3	24	26.2	24	87,000
"	20	16	36	27.6	85,000

At 406° the space velocity with catalyst (pumice-nickel-vanadium-oxide-sugar-charcoal) in Table IV is quite large and the resulting gases have composition comparable to that of carburetted water gas, the calorific value of the resulting gas mixture being somewhat less than carburetted water gas. This is due to the fact that the large amount of CO_2 present in the mixture acts merely as a diluent and if this could be removed by scrubbing, a gas of very high calorific value could be obtained.

The reactions taking place at the catalyst surface can be found out by a consideration of the composition of the incoming and effluent gases. It is clear that if reaction (2) were alone taking place, the percentage of carbon dioxide and methane would have been the same in the outflow gases. As a matter of fact the yield of methane is always greater than that of carbon dioxide. It thus appears that a part of the methane may have been produced by reaction (3). If these were the only two reactions taking place and if w , x , y and z be the respective volumes of CH_4 , CO_2 , CO and

H_2 in the outflow gases in a certain interval, then the incoming gases in that interval would consist of $(w+x+y)$ vol. of CO and the same volume of hydrogen. The volume of hydrogen used up therefore is $(w+x+y)-z$.

The quantity of hydrogen consumed in reaction (2) is $2x$ and that in reaction (3) is $3(w-x)$. Therefore $3(w-x)+2x$ should be equal to $(w+x+y)-z$. In many cases this equation holds good, indicating that an amount of methane equivalent to CO_2 is produced according to reaction (2) and the excess of methane by reaction (3). The last vertical column in Table IV gives the difference between the values of $(w+x+y)-z$ and $3(w-x)+2x$ for each of the experimental observations. It is evident from the table that this difference is generally very small.

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On Photochemical Reaction between Bromine and Tartaric Acid in Aqueous Solution.

Part I

BY

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AND

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Tartaric acid in bromine water yields hydrobromic acid, carbon dioxide and aldehydetartronic acid (Plotnikow, *Lehrbuch der Photochemie*, p. 576). This reaction was first studied in the dark by Bunsen and Roscoe (Ostwald's *Klassiker*, p. 92, No. 34, Photochemische Untersuchungen von Bunsen und Roscoe) who observed a very large period of induction as given in Table I below.

TABLE I

T(in hours)	18	20	42.5	88.5	163
$\frac{Bo-B}{Bo}$.01961	.02743	.05624	.43068	.62039

[($Bo-B$) gives the bromine that has passed into a state of combination.]

The experimental results obtained in this investigation suggest that the reaction between bromine and tartaric acid in presence of light is a complicated one.

EXPERIMENTAL ARRANGEMENT.

Pure tartaric acid was further purified by recrystallisation and was dissolved in conductivity water to the required strength. Bromine used in these experiments

was carefully purified by first crystallising out Merck's extra pure bromine and distilling the molten crystals over potassium bromide. The solutions were kept in the dark in resistance glass vessels and were used up almost as soon as they were prepared. Experimental results with solutions which have been allowed to stand for some time were rather erratic and different from those obtained with fresh solutions.

The source of light was a 1000 c. p. Pointolite lamp, the strength of the current and the voltage of which was maintained constant by means of a regulating resistance. A parallel beam of light was obtained by placing a lens at its focal distance from the lamp. An absorption vessel 4 c.m. thick containing N/50 CuSO₄ solution and a Wratten monochromatic filter (blue) gave a pure blue light of wave-length limits between 450-490 $\mu\mu$. The reaction cell was placed inside a double-walled metal box provided with a window to admit light from the lamp. Through the annular space of the box, water from a thermostat was circulated by means of a pump worked with a hot air motor. The temperature within the box was maintained constant within $\pm 0.1^\circ$. Solutions of tartaric acid and bromine were first allowed to take up the temperature of the thermostat and were then mixed inside the reaction cell. The quantity of bromine was measured iodometrically, at intervals.

The intensities of the incident and transmitted lights were measured by noting the deflections of a very sensitive galvanometer connected with a Johansen thermopile, placed behind the reaction cell containing (1) pure water and (2) the reaction mixture. The difference gives the amount of light absorbed. The galvanometer and the thermopile were calibrated by a Hefner lamp, which according to Gerlach, gives on a sq. cm. at a distance of 1 metre 900 ergs per second.

The Dark Reaction.—The velocity of the dark reaction at temperatures below 40° was found to be too small to be taken into account in studying the velocity and mechanism of the photochemical reaction. The photo-decomposition of water by bromine is also too slow to affect the results given in this article.

Induction Period.—Table II gives the data for the progress of the reaction at its initial stages.

TABLE II.

Strength of the incident blue light = 5400 ergs per sq. cm. per sec.

$$C_{Br_2} = 0.0325 \text{ N.}$$

$$C_{(\text{tartaric})} = 0.0666 \text{ M.}$$

2 c.c. of the solution titrated against 0.00404 N thiosulphate solution.

Temp. = $34^{\circ}\cdot 3$.

/ in minutes	0	15	30	45	60	80	196	256	331
C.c. of thio-sulphate soln.	16.1	16.1	15.95	15.45	15.1	13.8	10.5	9.5	8.4

Curve I in Fig. I gives the variation in concentration of Br_2 with time and in curve II the rate of transformation (not the velocity constant) is plotted against time. It will be seen that the rate of disappearance of bromine is at first very slow, reaches a maximum and then continually falls. For the descending limb of this curve, the reaction follows the unimolecular formula. This portion of the curve will be more thoroughly discussed later. No induction period was obtained when the reaction cell was exposed to intense sunlight or brought close to 1000 c.p. Pointolite lamp with only a water-filter interposed between. For incident light of average intensity,

however, a long induction period is always to be observed, which is practically independent of the concentration of either bromine or tartaric acid. These observations are in agreement with the classical experiments of Bunsen and Roscoe, who showed that for H_2 and Cl_2 mixture the induction period diminishes as the light intensity increases.

Table III gives experimental data, which enable the velocity constants corresponding to the descending limb of the curve to be calculated.

TABLE III.

Incident light intensity same as in Table II.

<i>t</i>	c.e. of thiosulphate.	Monomolecular <i>k</i> with conc. of Br_2 after 60 minutes' exposure as the initial concentration.	Monomolecular <i>k</i> with conc. of Br_2 after 150 minutes' exposure as initial concentration.
0	—	—	—
60	28.1	.00082	—
150	23.7	.00077	.000688
210	21.55	.00074	.000693
285	19.1	.00073	.000694
360	16.95		

It was noticed that for this particular light intensity, the induction period and all other initial disturbances were over in 120-150 minutes and thereafter the disappearance of bromine followed a monomolecular equation.

In Table IV are tabulated the velocity constants for various reaction mixtures, the initial concentration of bromine used for calculating the constants being the

concentration existing after two hours' exposure to blue light of intensity 5400 ergs per sec. per sq. cm.

TABLE IV.

Temp.= $34^{\circ}\cdot 3$.

Concentration of bromine in the original reaction mixture—0·0325 N.

Concentration of tartaric acid in the original reaction mixture	...	$\frac{2M}{3}$	$\frac{M}{3}$	$\frac{2M}{15}$	$\frac{M}{15}$
Monomolecular velocity coefficients	...	0043	00226	00118	00069

TABLE V.

Temp.= $34^{\circ}\cdot 3$.

Concentration of bromine in the original mixture—0·0147 N.

Concentration of tartaric acid in the original mixture	...	$\frac{M}{3}$	$\frac{2M}{15}$	$\frac{M}{15}$	$\frac{2M}{45}$
Monomolecular velocity coefficients	...	0126	00525	00278	00186

In the photochemical reaction between bromine and tartaric acid, there are two components, tartaric acid and bromine, of which the latter is photo-active. According to Plotnikow (*Lehrbuch der Photochemie*, p. 185), the velocity of the reaction should be expressed by the following equation :

$$\frac{d(b-x)}{dt} = \frac{kI_0}{p} \left[1 - e^{-ip(b-s)} \right] (a-x) \quad \dots \quad \dots \quad (1)$$

where a and b are the concentrations of tartaric acid and bromine respectively, I_0 the intensity of incident light and i the molecular extinction co-efficient. For very strong absorption equation (1) becomes

$$\frac{dx}{dt} = \frac{kI_0}{p}(a-x) \quad \dots \quad \dots \quad \dots \quad (2)$$

which is the equation for a monomolecular reaction. It is obvious that this equation, though monomolecular in form, cannot be applied to the experimental data for the simple reason that even when tartaric acid is in large excess compared to bromine (say, $M : .04 N$), a monomolecular constant is obtained; whereas if a is in large excess, $(a-x)$ is approximately constant and equation (2) transforms into a zero-molecular one.

For weak absorption of light, equation (1) becomes

$$\frac{dx}{dt} = kI_0 i(b-x)(a-x) \quad \dots \quad \dots \quad (3)$$

If a is in large excess, the reaction becomes unimolecular, but if b and a are comparable magnitudes, it retains its bimolecular character. If this equation were applicable it was to be expected that for large concentration of tartaric acid a monomolecular velocity constant would be obtained. The experimental results agree with this conclusion.

According to newer theories of the mechanism of a photochemical reaction, active molecules of the photo-active component are first produced by absorption of radiant energy. This activated molecule has a certain average life-period of excitation and if within this period, it can collide with an acceptor molecule, chemical transformation may occur. The probability of collision within the life-period of excitation (τ) will, in the cases of

gaseous systems, increase as the pressure of the acceptor gas molecules will increase, until for a very large concentration of the latter, all the activated molecules bring about chemical transformation by collision. The rate of chemical transformation for a constant rate of production of active molecules is given by

$$\frac{dc}{dt} = c \frac{\tau}{T + \tau} \quad \dots \quad \dots \quad \dots \quad (4)$$

Cairo, *Zeit Physik.*, 1922, 10, 185.

Turner, *Phys. Review*, 1924, 23, 466.

If, however, the rate of production of active molecules is not constant, as in our experiments, the amount of radiant energy absorbed depends on the concentration of bromine, the above equation should be modified thus :

$$\begin{aligned} \frac{dc}{dt} &= I_0 \left[1 - e^{-i(b-x)} \right] c \frac{\tau}{T + \tau} \\ &= (b-x)c' \frac{\tau}{T + \tau} \quad (\text{for weak absorption}) \end{aligned}$$

and the observed monomolecular velocity co-efficient,

$$k = c' \frac{\tau}{T + \tau} \quad \dots \quad \dots \quad \dots \quad (5)$$

Now the time period T between two successive collisions between an active bromine molecule and a tartaric acid molecule will, on the assumption that the kinetic theory of gases can be extended to dilute solutions, be given by the expression

$$T = \frac{1}{A \alpha \cdot p}$$

where

$$A = 2666 \cdot 6 \sqrt{\frac{2\pi N}{k\theta}} \cdot \frac{m_1 + m_2}{m_1 m_2}$$

a constant, a the distance between the centres of two reacting molecules on collision, and p the pressure of acceptor molecules expressed in millimeters of mercury (for solutions we may substitute osmotic pressure for gas pressure). It is obvious that in order that T should remain constant during the progress of the reaction, p should be kept constant. In our experiments tartaric acid was always in excess and its concentration remained practically constant. Then,

$$k = c' \frac{1}{1 + \frac{1}{Aa^2 \tau p}}$$

$$\frac{1}{k} = \frac{1}{c'} \left[1 + \frac{1}{Aa^2 \tau p} \right]$$

$$= \frac{1}{c'} + \frac{1}{Aa^2 \tau p c'} \dots \dots \quad (6)$$

Therefore $1/k$ plotted against $1/p$ should be a straight line. In Fig. 2 for curve II, where the initial concentration of bromine in the reaction mixture is $0 \cdot 0147 N$, this is true, but for curve I (for higher initial concentration of bromine) the line obtained is not straight.

It is clear from curve II (Fig. 2) and equation (6) that

$$\frac{\text{Intercept}}{\text{Slope}} = Aa^2 \tau$$

$$\text{Intercept} = 1 \cdot 4, \quad \text{slope} = \frac{9}{28 \times 10^{-6} \times \frac{3}{2}}$$

Now $A = 3 \cdot 09 \times 10^{21}$ and if $a = 3 \times 10^{-8}$,

τ becomes $2 \cdot 4 \times 10^{-11}$ seconds.

For curve I (Fig. II) the value of the intercept is the same as in curve II indicating that for infinite concentration of tartaric acid, the velocity constants will be the same independent of the concentration of bromine, but the slope generally is much greater than that of curve I, and therefore the life period of active bromine molecules for the higher initial concentration of bromine is less than for lower concentrations. The diminution in the velocity co-efficient with increase in the initial concentration of bromine, is thus traceable to the diminution in the life period of active bromine molecules.

Photochemical After-effect.—A mixture of 10 c.c. of 0·0975 N bromine solution and 20 c.c. of *M*/15 tartaric acid solution was exposed to bright sun-light for 5 minutes and then kept in the dark at 30°. It was found that the reaction progressed in the dark with very large velocity to begin with ; but in almost an hour's time the reaction stopped altogether. If the solutions of bromine and tartaric acid are exposed separately to sunlight and then mixed together in the dark, this dark reaction does not take place. The data are given in Table VI and the graph for the rate of transformation against time is plotted in Fig. I (curve III).

TABLE VI.

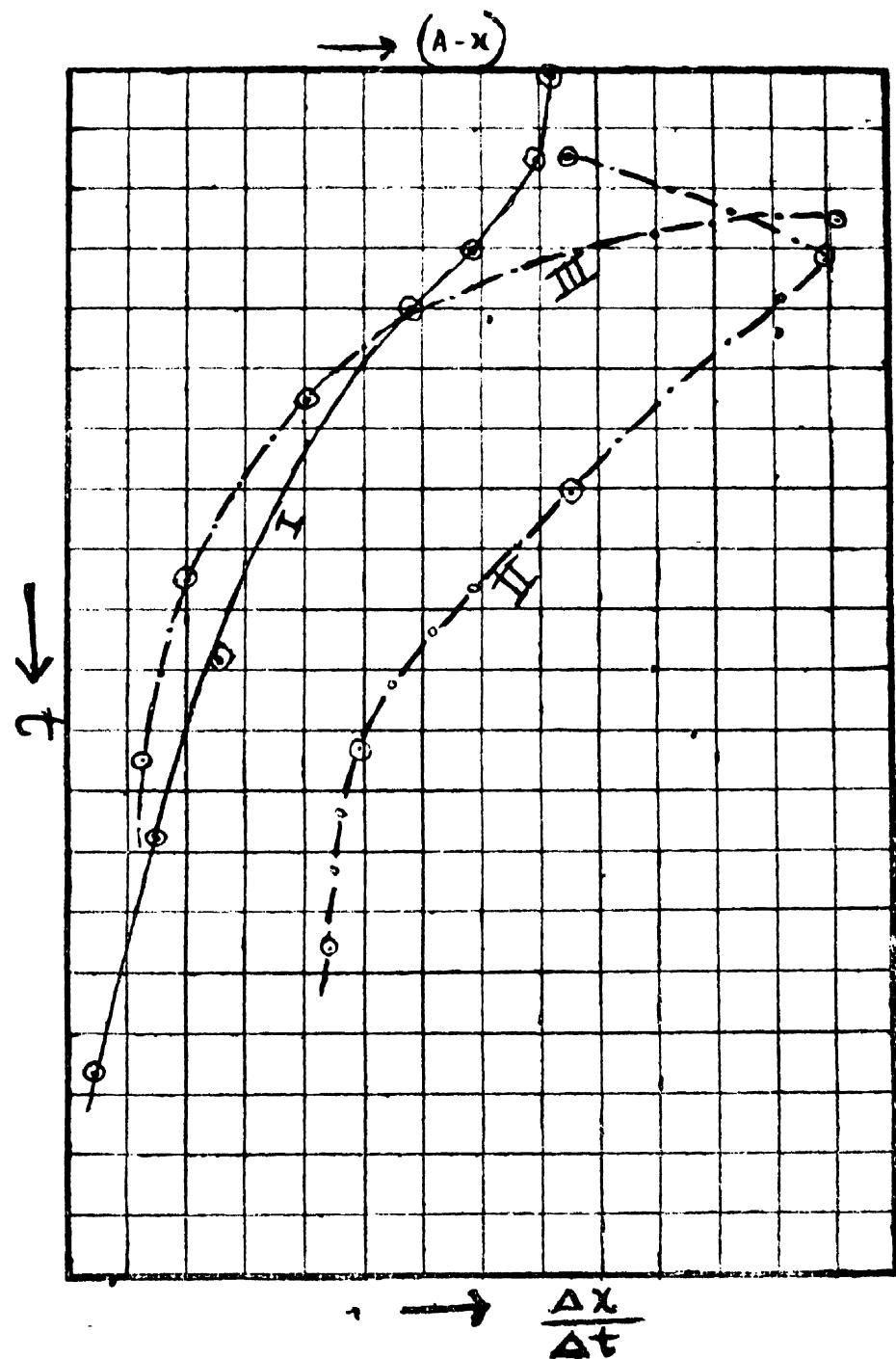
After 5 minutes' exposure to sunlight.

<i>t</i> (in minutes.)	C. c. of thiosulphate.	$k = \frac{1}{t} \log \frac{a}{a-x}$
0	7·9	·028
15	6·9	·024
30	6·6	·023
45	6·45	·025
60	6·35	—

It is thus clear that a compound of bromine and tartaric acid is formed when exposed to light, the bromine of this compound being available for iodometric titration. The free bromine (*i.e.*, bromine not in a state of combination with tartaric acid) can be determined from curve III (Fig. I) and is equivalent to 6.3 c.c. of thiosulphate solution. The concentration of the bromine-tartaric acid compound is at any time equivalent to the thiosulphate titre at that time minus 6.3 c.c. The velocity co-efficients in the third column of Table VI have been calculated in this way. It will be seen that the velocity co-efficient of this dark reaction (0.025) is very large compared to the observed velocity of photochemical reaction under similar conditions of concentrations, but at 34.3° (0.00069, see Table IV). It thus appears that the mechanism of this reaction consists in the formation of an intermediate compound between bromine and tartaric acid under the influence of light, the velocity of this reaction depending on the concentrations of bromine, tartaric acid, temperature and the intensity of light as given in Eq. (6) and Tables IV and V. The bromine of this intermediate compound is available for titration iodometrically. This intermediate compound decomposes in the dark giving CO_2 , HBr and aldehydetartronic acid, with a velocity constant very large compared with the velocity constant of the photochemical reaction in the first stage of transformation under the influence of the blue light of the intensity mentioned above. The theory of homogeneous consecutive reaction can, therefore, as usual, be applied to explain the observed period of induction.

Application of Einstein's Law of Photochemical Equivalence.

It is obvious from the large induction period that the reaction is a very complex one, which would not conform



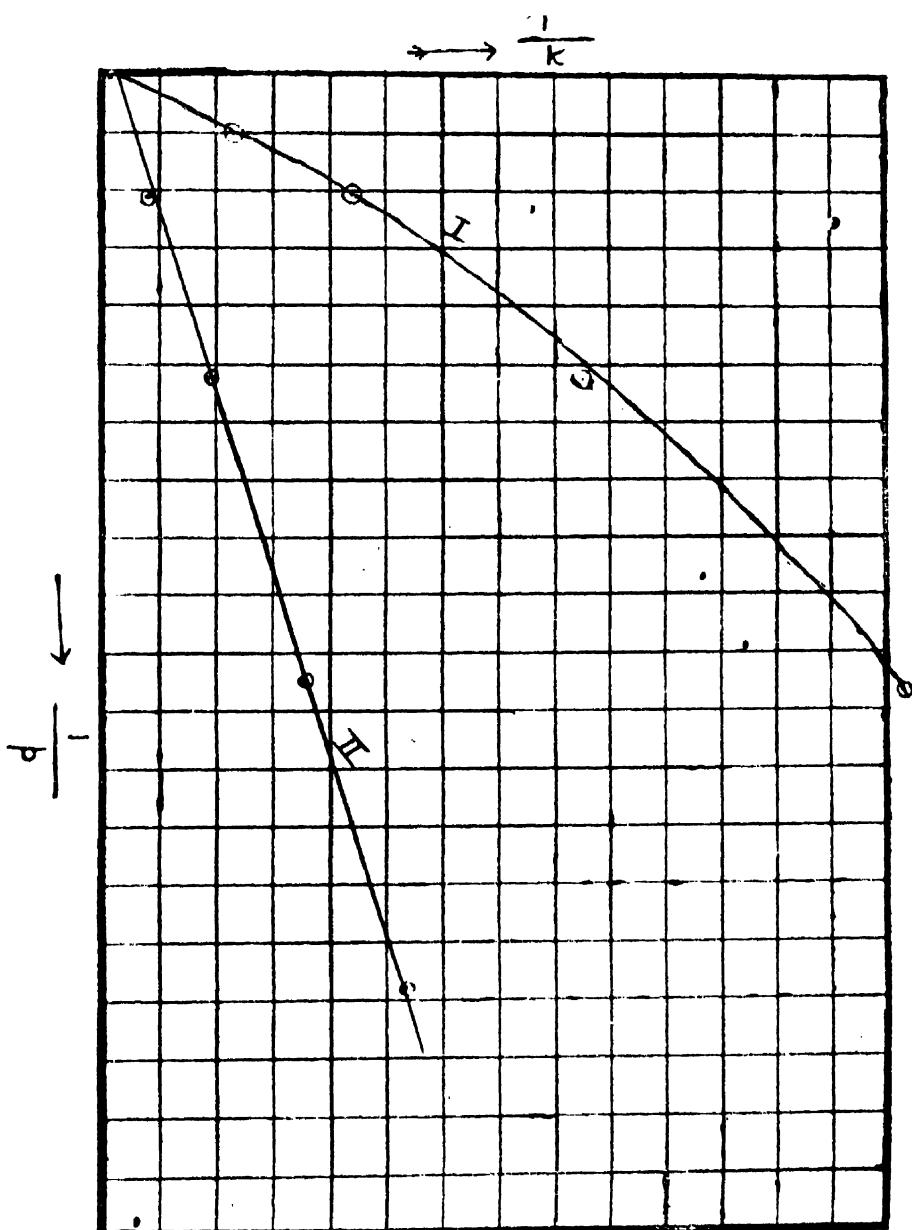


FIG. 2.

to Einstein's Law of Photochemical Equivalence. Still it was considered worthwhile to find out the total number of quanta that brings about the transformation of a molecule of bromine. The velocity of reaction, long after the induction period is over, should only be used for this calculation.

TABLE VII.

Temp. = $35^{\circ}\cdot 3$.Initial bromine concentration = $N/67$.Concentration of tartaric acid = $M/3$.

2 c.c. of the reaction mixture titrated against $M/995$ thiosulphate solution.

t in minutes	Quantity of thiosulphate required.
109	8.3
125	5 } mean 6.65

Intensity of blue light just behind the reaction vessels containing pure water is $\frac{8.6}{14} \times 900$ ergs per sec. per sq. cm.

Intensity of blue light just behind the reaction vessel filled with bromine solution, 2 c.c. of which = $6\cdot65$ c.c. of $M/995$ thiosulphate solution is $\frac{80\cdot41}{14} \times 900$ ergs per sec. per sq. cm.

Hence, quantity of light absorbed per sq. cm. per sec. is $\frac{5\cdot59}{14} \times 900$ ergs.

No. of quanta of blue light of average wave-length $470 \mu\mu$,

$$= \frac{5\cdot6}{14} \times 900 \times \frac{470 \times 10^{-7}}{6\cdot55 \times 10^{-27} \times 3 \times 10^{10}}.$$

No. of molecules of Br_2 transformed per c.c. (the reaction vessel was 1 cm. thick) per second.

$$= \frac{3 \cdot 3}{2} \times \frac{6 \cdot 17 \times 10^{23}}{990 \times 1000} \times \frac{1}{16 \times 60}$$

$$\frac{\text{No. of molecules}}{\text{No. of quanta absorbed}} = 12 \text{ (approx.)}$$

We have already seen that if the initial concentration of bromine is increased, the reaction velocity diminishes. It was found that for initial concentration of 0.0325 N bromine and of $2M/3$ tartaric acid the ratio of

$$\frac{\text{No. of mols}}{\text{No. of quanta}} = 4 \text{ (approx.).}$$

Velocity of Reaction in Plane Polarised and Circularly Polarised Light.

Tartaric acid is an optically active compound, and it was thought probable that the velocity of photo-bromination might not be dependent only on the intensity of light. A large nicol (4 sq. cm. in aperture) was used for obtaining the plane polarised light, whose intensities could be varied by using lenses of different focal lengths. A Fresnel Rhomb, interposed between the nicol and the reaction cell, gave circularly polarised light when the plane of polarisation of light incident normally on the face of the Rhomb, is at an angle of 45° to the horizontal cross-section of the Rhomb. To counteract the disturbing action, if any, of the film of Canada balsam on the nicol, the velocity of photo-bromination in ordinary light was also measured with a film of Canada balsam between two optical glass plates placed in front of reaction vessel.

	Divisions of Galvanometer.	Velocity Constant.
Intensity of parallel beam of ordinary light =	170	0.00489
Intensity of polarised light =	172	0.00493
Intensity of circularly pola- ris ed light =	155	0.0045

It thus appears that the velocity constant depends only on the intensity of light and is independent of the state of polarisation of the light.

Temperature Co-efficient of the Velocity of Reaction.

The majority of photochemical reactions have very small temperature co-efficients; in fact if Einstein's law were strictly correct the velocity should be independent of temperature. As Table VIII will show, the temperature co-efficient of this reaction is between 1.7 and 2.

TABLE VIII.

Temp.	Initial conc. of bromine.	Initial conc. of tartaric acid.	Velocity constant.
34°.3	.0325 <i>N</i>	<i>M</i> .15	.00069
24°.3	"	"	.00040
34°.3	.0137 <i>N</i>	"	.00284
24°.3	"	"	.0014.

Tolman (*J. Am. Chem. Soc.*, 1923, 45, 2285) has suggested a way out of this difficulty. He considers that molecules in the lower quantum state may not be in a condition to absorb radiant energy of the frequency used, or the energy level which they attain after the absorption

may not be high enough to lead to chemical reaction and obtains the relation

$$\frac{d \log K \text{ (velocity const.)}}{dT} = \frac{\bar{E} - E}{kT^2}$$

where \bar{E} is the average energy before activation of those molecules only which pick up radiant energy and react, and E is the average energy of all the molecules. If $\bar{E} - E$ is zero, the temperature co-efficient is unity but if $\bar{E} - E$ has a large value, the temperature co-efficient will be correspondingly large.

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Varying Valency of Platinum with respect to Mercaptanic Radicles.

Part II.

BY

SIR PRAFULLA CHANDRA RAY

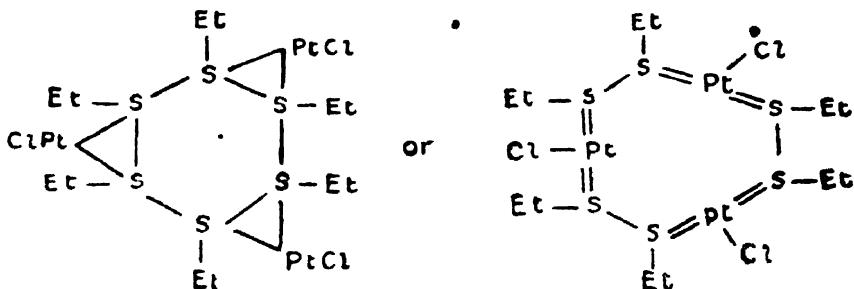
AND

KSHITISH CHANDRA BOSE RAY.

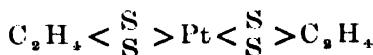
It has already been shown that platinum in relation to certain mercaptanic radicles behaves as di-, tri-, tetra-, penta-, hexa- and octa-valent respectively (*Ray J. Chem. Soc.*, 1923, 123, 133). In the present communication further evidence is brought forward in support of this view.

Tri-, Tetra- and Penta-valent Platinum.

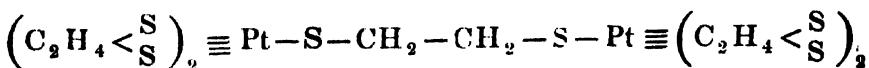
The product of the interaction of ethyl disulphide and platinic chloride, namely, $\text{Et}_2\text{S}_2\text{PtCl}$ has already been described (*loc. cit.*) in which the platinum has been assigned penta-valency. Determination of the molecular weight in chloroform has now led us to treble the empirical formula; platinum would thus function as tri- or penta-valent :



It will be seen that the second compound is a nine-membered ring in the formation of which platinum takes part. Both the rings also conform to the sulphonium type (*cf. J. Chem. Soc.*, 1916, 109, 131, 603; 1917, 111, 101, etc.). By the interaction of sodium dithioethylene glycol and platinic chloride in acetone, derivatives of the mercaptan have been obtained in which platinum functions as tetra- and penta-valent respectively, thus :



and

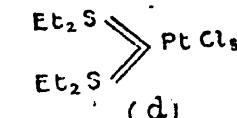
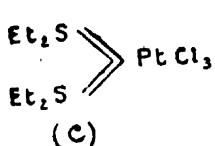
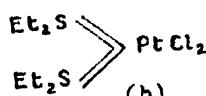
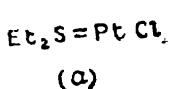


The motive of the reaction evidently lies in the affinity of sulphur for the metal, in other words, the latter readily parts with its halogen atoms in preference to the sulphur.

Interaction of Thylsulphide and Platinic Chloride.

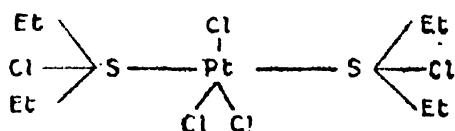
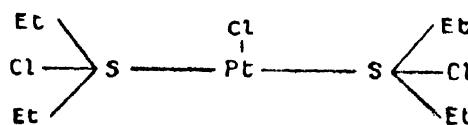
As early as 1853 Loir described the compound $(\text{Et}_2\text{S})_2\text{PtCl}_4$ which he obtained by the interaction of the above (*Ann. Chim. Phys.*, 1853, 39 [iii], 441). We have

recently undertaken a thorough and systematic investigation of the above reaction and have been able to isolate the following products of reaction : (a) $\text{Et}_2\text{S} \cdot \text{PtCl}_1$; (b) $(\text{Et}_2\text{S})_2 \cdot \text{PtCl}_2$; (c) $(\text{Et}_2\text{S})_2 \cdot \text{PtCl}_3$; (d) $(\text{Et}_2\text{S})_2 \cdot \text{PtCl}_4$ and (e) $(\text{Et}_2\text{S})_2 \cdot \text{PtCl}_5$. The compound (b) has been obtained in six different isomeric modifications. One form, m. p. 77° , has already been described (RÂy, *loc. cit.*). Two isomers with m.ps. 81° and 106° have been isolated by Blomstrand (*J. pr. Chem.*, 1888 [ii], 38, 352) both of which on further purification was shown by Tschugaeff and Malschewsky (*Zeit. anorg. Chem.*, 1924, 135, 385) to possess the identical m. p., namely, 108° . These two varieties appear to be identical with the compounds (a) and (γ) described below. Three more isomers with m. ps. 108° , 104° and 96° respectively have also been obtained. The various isomers differ distinctly in physical properties, such as colour, crystalline form, melting point and solubility. In one and the same reaction two, three or more products are often simultaneously formed but the predominance of the one over the others is determined by the temperature at which the reaction is carried on as also by the active mass of the reactants. With the exception of (e) these compounds may be arranged in the following order in which the affinity value of platinum continuously varies from tri- to octa-valency, thus :



But the existence of the compound $(\text{Et}_2\text{S})_2 \cdot \text{PtCl}_5$ would apparently land us in difficulty and is, in fact, a

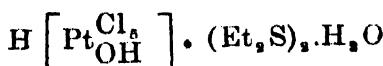
stumbling block in the path of the acceptance of the above method of representation of the valency of platinum, which would assign (*c*) hepta- and (*e*) ennea-valency. The following alternative mode of representation therefore naturally suggests itself :—



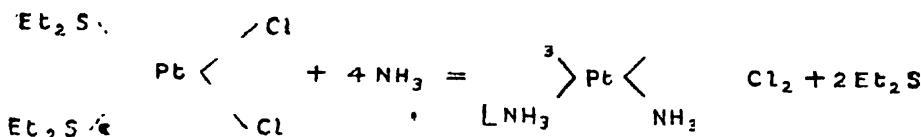
which would make platinum in (*c*) and (*e*) tri- and penta-valent respectively and sulphur tetravalent. This view of the constitution brings it into line with that proposed for Et_2S_2 , 2AuCl_2 in which the compound has been shown to belong to the sulphonium series (Rây, *J. Indian Chem. Soc.*, 1924, 1, 64). But a better method would be to explain their constitution according to Werner's theory. As for the different modifications of $(\text{Et}_2\text{S})_2\text{PtCl}_2$ the existence of three isomers can be explained in the following way :

- (1) Blomstrand's *cis*-compound;
- (2) Blomstrand's *trans*-compound;
- (3) $[\text{Pt}(\text{Et}_2\text{S})_4]\text{PtCl}_2$.

(*c*) may be represented as a molecular compound of (*b*) and (*d*): $[(\text{Et}_2\text{S})_2\text{PtCl}_2] [(\text{Et}_2\text{S})_2\text{PtCl}_4]$ or $[\text{Pt}(\text{Et}_2\text{S})_4]\text{PtCl}_6$ (*cf.* Tschugaeff, *Z. anorg. Chem.*, 1913, 82, 420). In fact on crystallisation from boiling alcohol, it breaks up into the two component molecules. (*e*) is constituted according to the scheme—



An aqueous solution of (*e*) turns blue litmus red, thus showing the acidic structure of the compound. This view of the constitution of these compounds receives further support from the facts that the following reaction takes place on treating (*b*) m. p. 96° and m. p. 104° with ammonia:



The ammonia-substituted compound has been found to precipitate the whole of its chlorine in aqueous solution with silver nitrate as silver chloride. Both the chlorine atoms are therefore outside the co-ordination ring. (c) when similarly treated with ammonia is converted into PtCl_2 , Et_2S , 4NH_3 . That the chlorine atoms in these compounds are not equally ionised in solution is proved by the conductivity experiments appended below as also by those made by Tschugaeff and Malschewsky (*loc. cit.*) Further work in this line is in progress.

EXPERIMENTAL.

Interaction of Disodium Dithioethyleneglycol and Platinic Chloride.—(a) The disodium compound was suspended in ether and solid platinic chloride was added. On being refluxed for a few hours a light brick-red precipitate was obtained, which was washed repeatedly with water till the filtrate was completely free from chlorine.

Found : Pt=43.93 ; S=29.14. Pt^{II} [Cl₂ : Pt(C₃H₅S₂)^{IV}] , (C₃H₅)₂O

or $\text{Pt}(\text{C}_5\text{H}_4\text{S}_2)_2$, PtCl_2 , $(\text{C}_5\text{H}_5)_2\text{O}^*$ requires $\text{Pt}=43.44$ and $\text{S}=28.22$ per cent.

* Cf. J. Indian Chem. Soc., 1924, 1. 79, foot-note.

(b) The disodium derivative was suspended in anhydrous acetone and an acetone solution of platinic chloride mixed with it. The mixture was refluxed on the water-bath for about an hour. A chocolate-coloured precipitate was obtained which was repeatedly extracted with boiling nitrobenzene in order to remove ethylene disulphide, which is produced simultaneously and which is deposited as a flocculent precipitate when the solvent cools down. The precipitate was finally washed with boiling alcohol

and ether. It had the composition $2\text{Pt}(\text{C}_2\text{H}_4\text{S}_2)_2$, $\text{C}_2\text{H}_4\text{S}_2$. (Found : Pt=46.11; S* = 35.00. Theory requires Pt=46.13 and S=37.50 per cent. Chlorine was found to be absent). When the same preparation was repeated by refluxing the mixture on the water bath for $1\frac{1}{2}$ hours, a precipitate was obtained which was purified by a method similar to that described above. The compound had the composition $(\text{C}_2\text{H}_4\text{S}_2)_2$ = Pt = $(\text{C}_2\text{H}_4\text{S}_2)_2$. (Found : Pt=49.61; C=12.43; H=2.40; S=33.73. Theory requires Pt=51.71; C=12.60; H=2.10 and S=33.60 per cent.) As platinic chloride is very sparingly soluble in ether the reaction was not completed in the sense that one atom of chlorine remained attached to the metal in the final product of the reaction ; whereas, when acetone was used as the menstruum in which platinic chloride is readily soluble the reaction went much further and the whole of the chlorine was removed.

Interaction of Diethylsulphide and Platinic Chloride.—

(a) Excess of aqueous chloroplatinic acid and ethylsulphide were heated in a sealed tube at 160° — 70° for 15 hours. On cooling, a treacle-like substance settled at the bottom of the tube ; it was separated from the supernatant

* As the sulphur was estimated by fusion with a mixture of sodium carbonate and potassium nitrate a small quantity of it escaped as sulphur. Hence the p. c. was found to be a little low (*vide infra*, foot-note, p. 185).

aqueous layer, dissolved in acetone and precipitated by alcohol. A brick-red product which did not melt up to 250° was obtained. It was further purified by crystallisation from a very concentrated solution in chloroform. (Found : Pt=61.75 ; Cl=11.18. $(C_2H_5)_2SPtCl$ requires Pt=61.09 and Cl=11.00 per cent). The acetone-alcoholic mother-liquor on evaporation gave a semi-solid mass which was repeatedly dissolved in chloroform and precipitated by ether. The crop of crystals thus yielded had the m. p. 108° (*vide infra*).

(b) Ethyl sulphide in excess and an aqueous solution of platinic chloride were mixed up in a sealed tube and heated in a steam-jacket for 5 hours. The aqueous supernatant layer was filtered off and allowed to evaporate spontaneously. The residue was treated with boiling alcohol and the solution filtered off. The filtrate on cooling deposited a crop of golden-yellow plates, m. p. 108° (α). (Found : Pt=44.50 ; Cl=16.47. $(Et_2S)_2PtCl_2$ requires Pt=43.97 and Cl=15.85 per cent.). The mother-liquor was allowed to evaporate. The residue was dissolved in hot benzene, which on cooling yielded a crop of pale white crystals, m. p. 108° (β). The aqueous layer described above on slow evaporation deposited pale greenish yellow crystals, m. p. 110° (γ). Though the compounds (α) and (β) had identical m. p. 108° they differed widely in physical properties such as colour, solubility and evidently crystalline form. This is quite in keeping with the constitution assigned to them according to Werner's theory as discussed above. All the varieties were analysed and were found to have the identical composition.

(c) Excess of ethylsulphide and solid platinic chloride were mixed in a test-tube and continuously stirred for about an hour. A pasty mass was obtained, which was treated with a few c.c. of water. The aqueous extract was removed by filtration. The pasty

mass was washed with alcohol so as to remove the unacted-upon ethylsulphide. The yellow residue was repeatedly washed with benzene till all the soluble impurities were removed. A bright orange-red crystalline mass was obtained, m. p. 109°. It had the composition $(Et_2S)_2PtCl_3$. (Found : Pt=41.47 ; Cl=22.09 and S*= 11.59. $(Et_2S)_2PtCl_3$ requires Pt=40.75 ; Cl=22.03 and S=13.24 per cent.). This product is evidently a 'molecular' compound made up of equimolecular proportions of (b) and (d), thus :



On crystallisation from boiling alcohol it yields a copious precipitate of (d). The mother-liquor on slow evaporation yields as first crop a mixture of (b) and (d) and the final crop is pure (b), m. p. 78°. The compound (d) had been prepared by another method and described in a previous communication (Rây, *J. Chem. Soc.*, 1923, 123, 140). On repeating the method of preparation described by Loir (*loc. cit.*) an orange-yellow crystalline precipitate was obtained. The French chemist described it as melting at 108° but the preparation, even on being repeated several times, was found to melt at 113°. Loir did not analyse this compound but thought—erroneously, as it is now found—that it could be further purified by crystallisation from boiling alcohol. By this process he only recovered the compound $(Et_2S)_2PtCl_4$ whose m. p.

* Great difficulty was experienced in estimating the sulphur of the present series of compounds. Carius' method followed by fusion with KNO_3 and Na_2CO_3 yielded negative results. The reason was that the Et_2S was thereby converted into the sulphone Et_2SO_2 . When the contents of the tube were washed out and evaporated to remove the excess of nitric acid, the sulphone volatilised with the steam and thus sulphur could not be estimated by this method. The nitric acid in Carius' method was therefore supplemented by the addition of bromine. The excess of bromine and nitric acid was subsequently evaporated off and the residue fused as usual with KNO_3 and Na_2CO_3 . Even this method gave the p. c. of sulphur slightly low.

he did not determine after recrystallisation. Evidently, the original compound $(Et_2S)_2PtCl_3$ broke up into its two components as shown above during the crystallisation.

(d) Ethylsulphide and an excess of an aqueous solution of platinic chloride were taken in a sealed tube and heated at 100° for 9 hours. On cooling, a yellow crystalline deposit was found at the bottom of the tube over which there was a layer of shining, colourless needle-shaped crystals. The tube was cut open and the two kinds of crystals filtered off from the aqueous mother-liquor, separated mechanically and pressed between the folds of a filter-paper to remove the adhering mother-liquor. The colourless variety had the m. p. 104° and the composition $(Et_2S)_2PtCl_2$ (δ). Evidently it was the fourth isomer of the compounds (α), (β) and (γ) described above. (Found: Pt = 44.35; Cl = 16.40 per cent.). The yellow crystals were purified by solution in hot alcohol, which on cooling deposited yellow needle-shaped crystals, m. p. 198° . This was identical with the compound (d). From the alcoholic mother-liquor of this product on spontaneous evaporation two sets of crystals were obtained: (i) lemon-yellow monoclinic plates, the crystallography of which is given below, and (ii) orange-yellow ill-defined needles. (i) was mechanically separated from (ii) and twice recrystallised from alcohol. This compound is the fifth isomer having the composition $(Et_2S)_2PtCl_2$, m. p. 96° (ϵ). (Molecular weight by the cryoscopic method in benzene = 336.3. Theory requires M.W. = 347.) The ebullioscopic method of M.W. determination in benzene gave anomalous results. Evidently some sort of molecular rearrangement takes place. (ii) was too minute in quantity to allow of purification and analysis. The aqueous mother-liquor in the above reaction was concentrated by slow evaporation over strong sulphuric acid whereby yellow crystals of a

mixture of $(Et_2S)_2PtCl_2$ and $(Et_2S)_2PtCl_4$ were obtained. These were filtered off and the mother-liquor further concentrated till no more yellow crystals were yielded. At this stage the filtrate, which became very small in bulk, was transferred to a lime-desiccator to remove HCl which began to evolve. Beautiful orange needle-shaped crystals began to separate out, which were further purified by redissolving in minute quantity of water. On repeating the process the pure crystals thus obtained were found to melt at 90° . They had the composition $(Et_2S)_2PtCl_5 \cdot 2H_2O$. (Found: Pt=33.96; Cl=30.42. Theory requires Pt=33.87 and Cl=30.06 per cent.)

Molecular Weight of $Et_2S_2 \cdot PtCl$.—Ebullioscopic determination of the molecular weight in chloroform gave M.W.=942. $(Et_2S_2 \cdot PtCl)_3$ requires M.W.=1093.5.

Conductivity of $(Et_2S)_2PtCl_4$ in Acetone Solution at 23° .

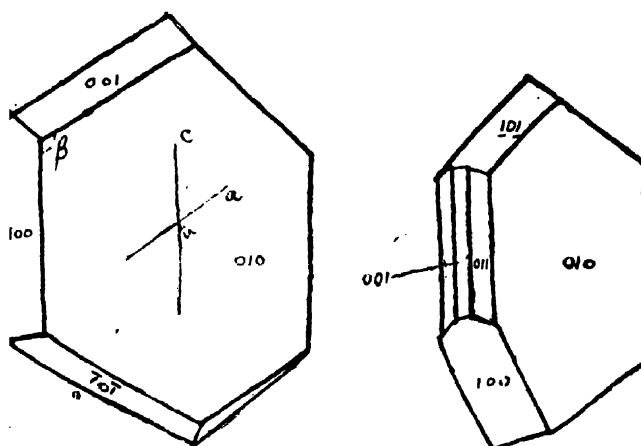
Concentration in gm. mols.	Specific conductivity $\times 10^{-9}$ (freshly prepared solution).	Sp. conductivity $\times 10^{-9}$ (after keeping the solution for 1 day).
0.01036	25.2	28.8
0.00518	12.2	14.8
0.00345	...	8.8

Conductivity of the Above at 30° .

Concentration in gm. mols.	Sp. cond. $\times 10^{-9}$ (freshly prepared solution).	Sp. cond. $\times 10^{-9}$ (after keeping for 1 day).	Sp. cond. $\times 10^{-9}$ (after keeping for 4 days).
0.0147	2.7	9.9	39.4
0.00885	...	4.6	20.0
0.00442	9.0
0.0089	...	6.1	19.2
0.00221	...	1.008	...

That the chlorine atoms are non-ionisable is afforded by the fact that on adding silver nitrate solution very slight precipitate of AgCl is obtained; but on shaking the mixture from day to day, the quantity of the latter goes on increasing. At the end of a fortnight complete precipitation is secured.

Crystallography of (d), m. p. 198°.



The crystals belong to monoclinic system, holohedral class.

Habit: (1) Pseudohexagonal, tabular on the clinopinacoid and also (2) stout prismatic.

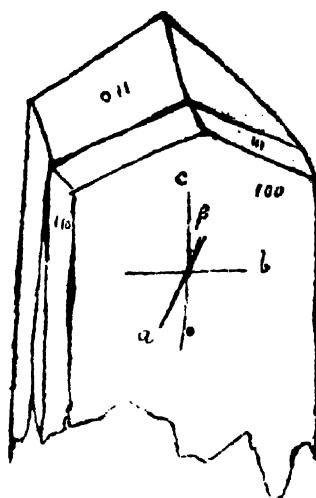
The following combination of forms is observed:—

(001)	Base
(010)	Clinopinacoid
(100)	Orthopinacoid
(110)	Unit prisms
(101)	Orthodome

Cleavage absent, conchoidal fracture: Highly brittle.

Optical Properties: Anisotropic, fairly strong double refraction with moderate interference colours. Faintly pleochroic. Extinction oblique. Ext. $\angle 12^\circ - 14^\circ$ on C-axis.

Crystallography of (ϵ), m. p. 96°.



The crystal belongs to the normal or holohedral class of the monoclinic system.

It has a pinacoidal habit—tabular on the orthopinacoid.

The following faces are the only ones present:—

Orthopinacoid	(100)
Clinodome	(011)
Unit prism	(110)
Unit pyramid	(111)

Cleavage planes totally absent. Fracture conchoidal.
Highly brittle.

Optically:—It is faintly pleochroic; the pleochroism is olive-green to brownish green.

Anisotropic, with fairly high birefringence.

Extinction oblique—extinction \angle on the C-axis is 10° — 11° .

No twinning present. Optically biaxial.

The crystal faces though fully developed, possess too imperfectly formed surfaces for goniometric treatment. Hence measurement of crystal angles and axes is impossible with such a crystal.

It is to be regretted that the crystals of the six modifications of $(Et_2S)_2PtCl_2$ were either of a mealy character or imperfectly developed. Only the (ϵ), m. p. 96° , could be obtained in a fairly perfect form. The compound (d) yielded, on slow evaporation from acetone solution, well-developed crystals.

Our thanks are due to Mr. D. N. Wadia of the Geological Survey of India who kindly undertook the crystallographic examination of the two samples.

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Received, May 8, 1925.

On the Nature of Hydrolytic Adsorption with reference to the Adsorption of Electrolytes and of Water.

Part I

General and Theoretical Introduction

BY

JNANENDRA NATH MUKHERJEE.

The nature of what is usually called "hydrolytic adsorption" has of late years attracted a good deal of attention. In a paper 'On the Adsorption of Ions' (Mukherjee, *Phil. Mag.*, 1922, 44 [VI], 330,) it was suggested that surfaces adsorbing neutral water molecules can react with acids and alkalis in solution. In another place (*loc. cit.*, p. 340-45) it was stated in connection with the origin of the latent acidity of sour soil that "the gel adsorbs anions by chemical affinity. The anions may be—

(1) of organic acids, such as humus acid;

(2) of simple electrolytes like chlorides, sulphates, carbonates, etc.

(3) hydroxyl ions from water.

Owing to the complex chemical nature of the gel and the enormous specific surface of the gels large quantities of anions may be adsorbed. An equivalent number of cations remain near the surface as the mobile second sheet or as electrically adsorbed. The exchange of bases is

simply due to the displacement of these ions, when the displacement is quantitative, equivalent amounts are exchanged. The anions primarily adsorbed or the cations in the second sheet are not of one kind. The relative numbers and chemical natures of these ions will evidently vary with different soils. An extract with a neutral salt can only be acid when the cations displaced from the second sheet (or electrically adsorbed) contain hydrogen ions or such ions as aluminium, which hydrolyse in dilute aqueous solutions. * * * That sometimes considerable quantities of bases are exchanged should be referred to the enormous surface of these gels and that probably the surface is saturated with anions. As crystalloids (insoluble) are also present, the type of exchange considered by Paneth (*loc. cit.*) is also possible. It is needless to point out that in the discussion only the theoretically simple case has been considered. Complications due to simultaneous primary adsorption and their mutual displacement are not always negligible. Besides the changes may not be restricted to the surface, formation of solid solutions, etc., are not excluded. Considering all these complex influences, it is interesting to note that most of the observed regularities correspond to the theoretically simple case."

The nature of the exchange of bases was also explained from the point of view of the exchange of adsorbed ions with those in solution.

In the present paper the theoretical considerations have been further elaborated and a brief summary has been given of the experimental evidence obtained in this laboratory during the last 4 years in support of the theory. The experimental portion together with a discussion of alternative explanations will be published in a series of papers dealing with individual systems.

General Remarks.

We shall apply the term 'hydrolytic adsorption' to cases where acids or alkalis are liberated by the interaction between solutions of salts having a neutral reaction and insoluble substances which do not give an acid or alkaline extract with water. We would also restrict the use of this term to cases where a simple chemical reaction between stoichiometric quantities cannot account for the facts, or in other words, the facts do not warrant a representation in terms of reactions between molecules with definite molecular weights.

It is apparent that if the reaction of the solution of the neutral salt after contact with the insoluble phase becomes acid, a corresponding quantity of base must separate and remain associated with the insoluble phase. Also it is scarcely necessary to mention that such a splitting up of a salt into an acid and a base involves either of three possibilities, namely,

(1) an interaction between the salt and water molecules (primarily) adsorbed on the surface, or,

(2) the direct or indirect replacement of hydrogen ions present in the surface layer by a cation present in the solution, or,

(3) the direct or indirect replacement of hydroxyl ions in the surface layer by anions in solution.

In order to explain the nature of hydrolytic adsorption it is not sufficient to say that 'hydrolytic' separation of the constituents of the salt has taken place as a result of adsorption. It is merely a statement of what has happened, unless we can define the nature of the adsorption process and can give a more or less definite picture of the changes in the surface layer. From the point of view adopted in this and previous papers (*Phil. Mag.*, loc. cit.;

Fdr. Soc. Disc., Oct., 1920; Published as *The Physics and Chemistry of Colloids*, Apl., 1921; *J. Chem. Soc.*, 1924, 125, 476; *J. Indian Chem. Soc.*, 1924, 1, 173,) it is possible to imagine several types of reactions which will lead to the liberation of acids or alkalis when a neutral (salt) solution is brought in contact with an insoluble phase.

We have formulated them under the heads A, B, C and D. The experimental evidence in support of each type is briefly stated under each head.

A. *Interaction between a Neutral Electrolyte and Adsorbed Acids of which the Anion is Primarily Adsorbed by the Adsorbent.*

(1)

As a special case of this type of reaction let us assume that the adsorbent is an insoluble salt BA where the base BOH and the acid HA are both strongly ionised in their solutions. Suppose now that the insoluble salt BA under certain conditions of precipitation develop a large amount of specific surface * and that it can also adsorb a considerable quantity of the acid HA'. The extent of adsorption will evidently depend on the nature of the adsorbent and on that of the acid as also on the concentration of the acid.

Let us now further suppose that the adsorbent does not adsorb the molecules of the acid as such but that the anions A' are 'primarily adsorbed' on the surface in virtue of the chemical affinity of the atoms on the surface in the sense in which the term has been used by the writer in previous papers.

The system composed of the adsorbent BA and the adsorbed acid HA' will have from our point of view the following characteristic properties :—

* The amount adsorbed per unit surface, we have reasons to think, also varies with the conditions of preparation.

(i) If the adsorption of anions be very intense it will be difficult to wash out the last trace of the adsorbed acid and in suitable cases it will be possible to show that the substance retains adsorbed acid even after repeated washings with pure water.

Usually, however, on long continued washing the adsorbed substance will come out continuously till it is completely removed.

(ii) The adsorption of the anion will impart a negative charge to the surface. This will not be the case if neutral molecules as such are adsorbed on the surface or if the constituent ions of the electrolyte remain in the 'primarily' absorbed layer.

The increase in negative charge will, when the adsorption of the cation is not very prominent, be noticeable at low electrolyte concentrations. At higher concentrations the 'electrical adsorption' of the cation will predominate and a lowering of the negative charge will be observed.

(iii) It might also be pointed out in this connection that the amount so adsorbed is usually small because the primarily adsorbed layer is formed through what might be called a sort of chemical combination and is determined by the number of places on the surface where adsorbed molecules can be 'fixed' up. *The adsorbent has thus a 'saturation capacity' determined by the number of such places per unit surface.* For a given sample of an adsorbent prepared under identical conditions a definite amount of an anion will be necessary to saturate unit surface.

(iv) *If only the anions A' are primarily absorbed, equal amounts of different electrolytes containing the same anion but different cations will be adsorbed, when the effective anion concentration (or rather activity) remains the same.* Moreover, this condition will be satisfied only when the surface exerts no chemical affinity on the cations.

(v) Since the forces acting between the charged surface and the cations in the mobile layer are mainly electrical in nature the freely moving hydrogen ions will be easily replaceable by other cations of neutral salts. The amount of acids liberated by neutral salts will depend on the amount of replaceable hydrogen ions (which in its turn is determined by the amount of anions remaining primarily adsorbed), on the concentration (or activity) of the cation of the salt, and on the relative (electrical and chemical) adsorbability and mobility of the cation.

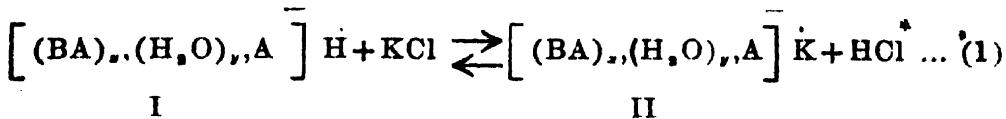
Here also we have assumed that the anion of the salt which has been added is not adsorbable by the surface—an assumption which is not true in all cases.

(vi) It is evident that the system is acting like an acid in the sense that it has got replaceable hydrogen ions. *The essential difference from the ordinary conception of an acid is that the adsorbent need not at all be 'acidic' or 'basic' in character and that the 'acidity' may be due to the adsorption of acid, resulting from the primary adsorption of anions.* Consequently there is no definite and simple stoichiometric relationship between the amount of the adsorbent and the amount of replaceable hydrogen ions, and as stated before, the ratio of the amounts of replaceable hydrogen ions to the mass of the adsorbent depends on the mode of preparation and on the adsorbability of the anion.

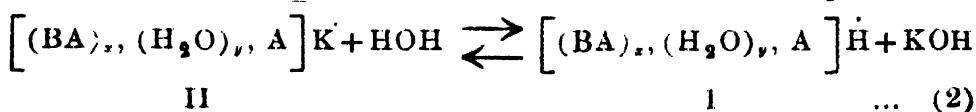
Moreover, the quantitative relationships between the concentrations of interacting ions are governed by the considerations set forth in this and previous papers and not by the usual conceptions applicable to the case of molecularly dissolved acids.

(vii) The system BA with adsorbed acids, on treatment with the solution of a neutral salt, will evidently be converted into a system containing adsorbed salts. The reaction may be represented as follows *assuming that all*

the hydrogen or potassium ions are in the mobile sheet of the double layer :



(viii) Depending on the relative adsorbabilities and concentrations of potassium and hydrogen ions the substance II may be partially converted into the substances I when brought in contact with pure water liberating the corresponding alkali as represented below :—



The above reaction is the counterpart of the usual type of hydrolysis.

The total amount of alkali so liberated will depend on the amount of potassium in II, on the relative adsorbabilities of hydrogen and potassium ions and on the concentration of hydrogen ions. The concentration of the liberated alkali will depend on the ratio of the two ions in the double layer.

(2) Other Adsorbents.

The general case where the adsorbent need not be polar in character does not need further comment except

* The surface is usually hydrated, the quantity of water hydrating the surface is represented by γ grammoles per x grammoles of the solid adsorbent—the gram molecular wt. of the adsorbent may be taken to be that corresponding to the simple chemical formula for the purpose of representing the quantities involved. The solid substances I and II are not totally different in the sense that only the composition and the double layer changes. On the addition of the solution of potassium chloride some of the hydrogen ions in the double layer are replaced by an equivalent number of potassium ions.

that, as we shall see presently, the 'acidic' or 'basic' character of an adsorbent will determine the nature of the anion which will be 'primarily' adsorbed. An adsorbent which will show a marked capacity to adsorb primarily hydroxyl ions, or, in other words, to react with hydroxyl ions in virtue of the chemical character of the atoms on the surface, will evidently be 'acidic' in character. A 'basic' adsorbent will show a marked capacity to adsorb primarily, that is, to react with hydrogen ions. Now these are the constituent ions of water and as it is well-known from the effect of even very low concentrations of electrolytes on electro-osmosis, cataphoresis and allied phenomena that hydrogen and hydroxyl ions are likely to be adsorbed from water in appreciable quantities in suitable cases. For the sake of convenience the adsorption of hydroxyl ions (a special case of 'anion adsorption) and of hydrogen ions (a special case of cation adsorption) will be dealt with in a separate section.

B. Interaction between a Neutral Electrolyte and adsorbed Alkali of which the Cation is Primarily Adsorbed by the Adsorbent.

This case also does not require any detailed consideration as the criteria enumerated above are all equally applicable with the difference that the adsorption of a cation will increase the positive charge of the surface and that the mobile sheet will consist of anions (hydroxyl ions in the case of alkalis). It may be pointed out here that the alkali metal ions do not seem to be 'primarily' adsorbable (Mukherjee and Roy, *J. Chem. Soc., loc. cit.*) The replacement of hydroxyl ions by other anions will be more complicated as chemical affinity between the surface and the replacing anions has to be taken into account.

Experimental Evidence in support of Reactions Formulated under A and B.

It is well-known that polar precipitates adsorb electrolytes. Recently Weiser and Sherrich (*J. Phys. Chem.*, 1919, 23, 205,) have found that precipitates of barium sulphate strongly adsorb electrolytes. For this reason this precipitate was first chosen for our experiments. A summary of the main results obtained in collaboration with Mr. J. K. Basu is given below.

Experiments with Barium Sulphate.

Weiser and others have shown that marked adsorption occurs when the medium in which the insoluble salt is precipitated contains the electrolytes. We have also found this to be the case. Precipitations of barium sulphate were carried on in presence of the following acids :—hydrochloric, acetic, phosphoric, citric, tartaric and sulphuric. The precipitate was washed repeatedly with pure water having a ρ_H between 6.4 to 6.6 at 28°, till the washed water is free from acid as shown by a ρ_H value between 6.2 to 6.4. Two equal portions of the precipitate are then left in contact with saturated potassium chloride and water respectively for 24 hours. There were no extraneous sources of acids and alkalis in these experiments.

(1) After contact with the neutral salt a marked acid reaction ranging up to a ρ_H value of 2.2 and mostly lower than 4.6 is observed in the potassium chloride solution. The water of the parallel experiment does not show (when the proper care in washing has been taken) a ρ_H value lower than 5.8. If the potassium chloride solution is replaced by a fresh volume of the solution, acid is again liberated but the ρ_H of successive extracts increases in value and is to be referred to a decrease in the ratio of hydrogen to potassium ions in the double layer.

* The samples used always liberate small quantities of acids in contact with water. This explains why, on treatment with potassium chloride solution, traces of adsorbed anions are also liberated as also the fact that, on patient long-continued washing, the adsorbed electrolyte can be removed almost completely so that no such marked acid reaction develops in contact with potassium chloride solution.

(2) But when the precipitation takes place in presence of alkalis the well-washed precipitate liberates only slightly higher concentration of alkalis in contact with neutral potassium chloride solution, than in contact with water. The maximum alkalinity observed is a p_H value equal to 8 only while the water of the parallel experiment shows a p_H value equal to 7.2. This is to be expected as the alkali metal ions (sodium and potassium hydroxides have been used) are not primarily adsorbed. Only a few mobile hydroxyl ions are probably present having as their partner the outermost layer of barium ions lying on the surface.

(3) At low concentrations the solution of the alkali salts of these acids increase, in the cases so far studied, the negative charge of surface.

(4) The adsorption of acids can be shown analytically (*cf.* Weiser and others, *loc. cit.*).

(5) The amount of acid liberated in presence of neutral salts is not determined by the weight of barium sulphate used but depends on the conditions under which adsorption has taken place. Thus the experiments when repeated with barium sulphate precipitated from equivalent quantities of barium chloride and potassium sulphate in the absence of acids and subsequently washed carefully with water though showing similar results liberate much smaller amounts of acid with potassium chloride. This fact shows that much greater adsorption takes place during

precipitation and that the ratio of the amount of replaceable hydrogen ions to the mass of the adsorbent varies with the conditions of preparation of the adsorbent.

(6) The ease with which the hydrogen ions are replaced by alkali metal cations (an acid reaction is developed immediately on mixing) and the negative charge show that they exist mostly in the mobile layer.

Experiments have been done with barium sulphate using neutral salts other than potassium chloride and similar results have been observed.

Experiments with other Polar Precipitates

The insoluble salts mentioned below have also been investigated. The precipitation took place in the presence of acids. The liberation of alkalis by neutral salts is very small in those cases where the experiments could be carried out with alkalis instead of acids. The precipitates used were barium chromate, lead sulphate, lead chromate, lead iodate, silver chloride, silver bromide, silver chromate, silver iodide and strontium sulphate.

The lead and silver salts with adsorbed acids do not give an acid extract with potassium chloride but liberate acids in contact with a solution of barium chloride. ρ_H changes from 6.2 to 5, the ρ_H of the blank containing water changes from 6.4 to 5.8 showing that barium ions can replace hydrogen ions with greater facility than potassium ions can. The failure to obtain an acid extract with potassium chloride is probably also due to the small amount of the acid that remain adsorbed when the sample is washed carefully.

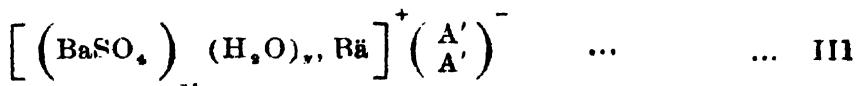
These experiments leave on doubt as to the existence of the type of reaction formulated by the writer. A much more interesting and in a sense novel result has been obtained in the course of these experiments.

C. Generation of Acids or Alkalies during Precipitation of Barium Sulphate from 'neutral' Salt Solutions.

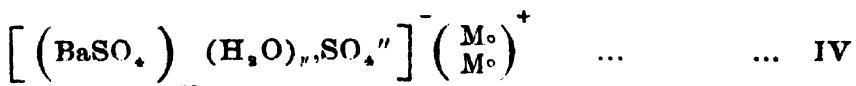
The writer along with Fajans (Mukherjee, *J. Indian Chem. Soc.*, 1924, 1, 173, and references to literature given therein) have emphasised the strong adsorption of a constituent ion by a polar precipitate. A precipitate like barium sulphate can be expected to adsorb barium and sulphate ions strongly. It has been found that (1) when precipitated by an excess of potassium sulphate from barium chloride the surface adsorbs sulphate ions. Their presence in the surface can be shown from electro-osmotic or cataphoretic experiments. The precipitate is negatively charged. (2) Similarly when precipitated from excess of barium chloride the surface becomes positively charged.

(3) The adsorption of electrolytes can also be shown analytically. Here, therefore, we get two systems resulting from the adsorption of electrolytes by the same adsorbent one of which is positively charged and the other negatively charged, i.e., the primarily adsorbed ion is a cation in the one case and an anion in the other case.

The two systems may be represented as follows :—



and



Systems III and IV have easily replaceable anions and cations respectively as these ions constitute the mobile layer of ions. On treatment with neutral salts, the anions will be replaced in system III and the cations in system IV. This has been observed to be the case. It must however be stated, as has already been pointed out, that the adsorbed electrolyte comes out in traces on washing

(i) If the adsorption of anions be very intense it will be difficult to wash out the last trace of the adsorbed acid and in suitable cases it will be possible to show that the substance retains adsorbed acid even after repeated washings with pure water.

Usually, however, on long continued washing the adsorbed substance will come out continuously till it is completely removed.

(ii) The adsorption of the anion will impart a negative charge to the surface. This will not be the case if neutral molecules as such are adsorbed on the surface or if the constituent ions of the electrolyte remain in the 'primarily' absorbed layer.

The increase in negative charge will, when the adsorption of the cation is not very prominent, be noticeable at low electrolyte concentrations. At higher concentrations the 'electrical adsorption' of the cation will predominate and a lowering of the negative charge will be observed.

(iii) It might also be pointed out in this connection that the amount so adsorbed is usually small because the primarily adsorbed layer is formed through what might be called a sort of chemical combination and is determined by the number of places on the surface where adsorbed molecules can be 'fixed' up. *The adsorbent has thus a 'saturation capacity' determined by the number of such places per unit surface.* For a given sample of an adsorbent prepared under identical conditions a definite amount of an anion will be necessary to saturate unit surface.

(iv) *If only the anions A' are primarily absorbed, equal amounts of different electrolytes containing the same anion but different cations will be adsorbed, when the effective anion concentration (or rather activity) remains the same. Moreover, this condition will be satisfied only when the surface exerts no chemical affinity on the cations.*

(v) Since the forces acting between the charged surface and the cations in the mobile layer are mainly electrical in nature the freely moving hydrogen ions will be easily replaceable by other cations of neutral salts. The amount of acids liberated by neutral salts will depend on the amount of replaceable hydrogen ions (which in its turn is determined by the amount of anions remaining primarily adsorbed), on the concentration (or activity) of the cation of the salt, and on the relative (electrical and chemical) adsorbability and mobility of the cation.

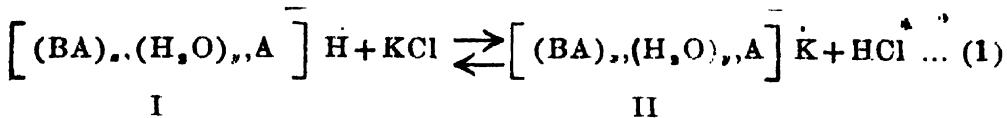
Here also we have assumed that the anion of the salt which has been added is not adsorbable by the surface—an assumption which is not true in all cases.

(vi) It is evident that the system is acting like an acid in the sense that it has got replaceable hydrogen ions. *The essential difference from the ordinary conception of an acid is that the adsorbent need not at all be 'acidic' or 'basic' in character and that the 'acidity' may be due to the adsorption of acid, resulting from the primary adsorption of anions.* Consequently there is no definite and simple stoichiometric relationship between the amount of the adsorbent and the amount of replaceable hydrogen ions, and as stated before, the ratio of the amounts of replaceable hydrogen ions to the mass of the adsorbent depends on the mode of preparation and on the adsorbability of the anion.

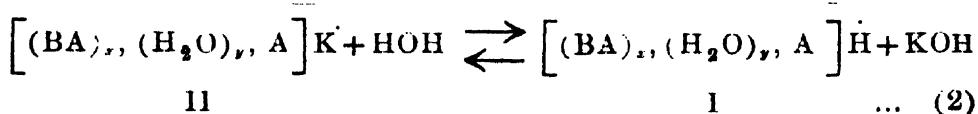
Moreover, the quantitative relationships between the concentrations of interacting ions are governed by the considerations set forth in this and previous papers and not by the usual conceptions applicable to the case of molecularly dissolved acids.

(vii) The system BA with adsorbed acids, on treatment with the solution of a neutral salt, will evidently be converted into a system containing adsorbed salts. The reaction may be represented as follows *assuming that all*

the hydrogen or potassium ions are in the mobile sheet of the double layer :



(viii) Depending on the relative adsorbabilities and concentrations of potassium and hydrogen ions the substance II may be partially converted into the substances I when brought in contact with pure water liberating the corresponding alkali as represented below :—



The above reaction is the counterpart of the usual type of hydrolysis.

The total amount of alkali so liberated will depend on the amount of potassium in II, on the relative adsorbabilities of hydrogen and potassium ions and on the concentration of hydrogen ions. The concentration of the liberated alkali will depend on the ratio of the two ions in the double layer.

(2) Other Adsorbents.

The general case where the adsorbent need not be polar in character does not need further comment except

* The surface is usually hydrated, the quantity of water hydrating the surface is represented by γ grammoles per x grammoles of the solid adsorbent—the gram molecular wt. of the adsorbent may be taken to be that corresponding to the simple chemical formula for the purpose of representing the quantities involved. The solid substances I and II are not totally different in the sense that only the composition and the double layer changes. On the addition of the solution of potassium chloride some of the hydrogen ions in the double layer are replaced by an equivalent number of potassium ions.

that, as we shall see presently, the 'acidic' or 'basic' character of an adsorbent will determine the nature of the anion which will be 'primarily' adsorbed. An adsorbent which will show a marked capacity to adsorb primarily hydroxyl ions, or, in other words, to react with hydroxyl ions in virtue of the chemical character of the atoms on the surface, will evidently be 'acidic' in character. A 'basic' adsorbent will show a marked capacity* to adsorb primarily, that is, to react with hydrogen ions. Now these are the constituent ions of water and as it is well-known from the effect of even very low concentrations of electrolytes on electro-osmosis, cataphoresis and allied phenomena that hydrogen and hydroxyl ions are likely to be adsorbed from water in appreciable quantities in suitable cases. For the sake of convenience the adsorption of hydroxyl ions (a special case of anion adsorption) and of hydrogen ions (a special case of cation adsorption) will be dealt with in a separate section.

B. Interaction between a Neutral Electrolyte and adsorbed Alkali of which the Cation is Primarily Adsorbed by the Adsorbent.

This case also does not require any detailed consideration as the criteria enumerated above are all equally applicable with the difference that the adsorption of a cation will increase the positive charge of the surface and that the mobile sheet will consist of anions (hydroxyl ions in the case of alkalis). It may be pointed out here that the alkali metal ions do not seem to be 'primarily' adsorbable (Mukherjee and Roy, *J. Chem. Soc., loc. cit.*) The replacement of hydroxyl ions by other anions will be more complicated as chemical affinity between the surface and the replacing anions has to be taken into account.

Experimental Evidence in support of Reactions Formulated under A and B.

It is well-known that polar precipitates adsorb electrolytes. Recently Weiser and Sherrich (*J. Phys. Chem.*, 1919, 23, 205,) have found that precipitates of barium sulphate strongly adsorb electrolytes. For this reason this precipitate was first chosen for our experiments. A summary of the main results obtained in collaboration with Mr. J. K. Basu is given below.

Experiments with Barium Sulphate.

Weiser and others have shown that marked adsorption occurs when the medium in which the insoluble salt is precipitated contains the electrolytes. We have also found this to be the case. Precipitations of barium sulphate were carried on in presence of the following acids :—hydrochloric, acetic, phosphoric, citric, tartaric and sulphuric. The precipitate was washed repeatedly with pure water having a ρ_H between 6.4 to 6.6 at 28° , till the washed water is free from acid as shown by a ρ_H value between 6.2 to 6.4. Two equal portions of the precipitate are then left in contact with saturated potassium chloride and water respectively for 24 hours. There were no extraneous sources of acids and alkalis in these experiments.

(1) After contact with the neutral salt a marked acid reaction ranging up to a ρ_H value of 2.2 and mostly lower than 4.6 is observed in the potassium chloride solution. The water of the parallel experiment does not show (when the proper care in washing has been taken) a ρ_H value lower than 5.8. If the potassium chloride solution is replaced by a fresh volume of the solution, acid is again liberated but the ρ_H of successive extracts increases in value and is to be referred to a decrease in the ratio of hydrogen to potassium ions in the double layer.

The samples used always liberate small quantities of acids in contact with water. This explains why, on treatment with potassium chloride solution, traces of adsorbed anions are also liberated as also the fact that, on patient long-continued washing, the adsorbed electrolyte can be removed almost completely so that no such marked acid reaction develops in contact with potassium chloride solution.

(2) But when the precipitation takes place in presence of alkalis the well-washed precipitate liberates only slightly higher concentration of alkalis in contact with neutral potassium chloride solution, than in contact with water. The maximum alkalinity observed is a p_H value equal to 8 only while the water of the parallel experiment shows a p_H value equal to 7.2. This is to be expected as the alkali metal ions (sodium and potassium hydroxides have been used) are not primarily adsorbed. Only a few mobile hydroxyl ions are probably present having as their partner the outermost layer of barium ions lying on the surface.

(3) At low concentrations the solution of the alkali salts of these acids increase, in the cases so far studied, the negative charge of surface.

(4) The adsorption of acids can be shown analytically (*cf.* Weiser and others, *loc. cit.*).

(5) The amount of acid liberated in presence of neutral salts is not determined by the weight of barium sulphate used but depends on the conditions under which adsorption has taken place. Thus the experiments when repeated with barium sulphate precipitated from equivalent quantities of barium chloride and potassium sulphate in the absence of acids and subsequently washed carefully with water though showing similar results liberate much smaller amounts of acid with potassium chloride. This fact shows that much greater adsorption takes place during

precipitation and that the ratio of the amount of replaceable hydrogen ions to the mass of the adsorbent varies with the conditions of preparation of the adsorbent.

(6) The ease with which the hydrogen ions are replaced by alkali metal cations (an acid reaction is developed immediately on mixing) and the negative charge show that they exist mostly in the mobile layer.

Experiments have been done with barium sulphate using neutral salts other than potassium chloride and similar results have been observed.

Experiments with other Polar Precipitates

The insoluble salts mentioned below have also been investigated. The precipitation took place in the presence of acids. The liberation of alkalis by neutral salts is very small in those cases where the experiments could be carried out with alkalis instead of acids. The precipitates used were barium chromate, lead sulphate, lead chromate, lead iodate, silver chloride, silver bromide, silver chromate, silver iodide and strontium sulphate.

The lead and silver salts with adsorbed acids do not give an acid extract with potassium chloride but liberate acids in contact with a solution of barium chloride. ρ_H changes from 6.2 to 5, the ρ_H of the blank containing water changes from 6.4 to 5.8 showing that barium ions can replace hydrogen ions with greater facility than potassium ions can. The failure to obtain an acid extract with potassium chloride is probably also due to the small amount of the acid that remains adsorbed when the sample is washed carefully.

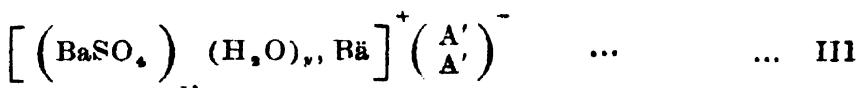
These experiments leave on doubt as to the existence of the type of reaction formulated by the writer. A much more interesting and in a sense novel result has been obtained in the course of these experiments.

C. *Generation of Acids or Alkalies during Precipitation of Barium Sulphate from 'neutral' Salt Solutions.*

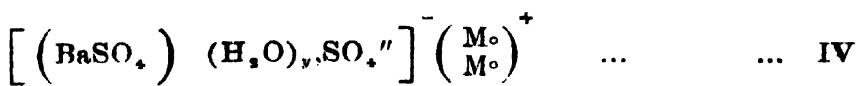
The writer along with Fajans (Mukherjee, *J. Indian Chem. Soc.*, 1924, 1, 173, and references to literature given therein) have emphasised the strong adsorption of a constituent ion by a polar precipitate. A precipitate like barium sulphate can be expected to adsorb barium and sulphate ions strongly. It has been found that (1) when precipitated by an excess of potassium sulphate from barium chloride the surface adsorbs sulphate ions. Their presence in the surface can be shown from electro-osmotic or cataphoretic experiments. The precipitate is negatively charged. (2) Similarly when precipitated from excess of barium chloride the surface becomes positively charged.

(3) The adsorption of electrolytes can also be shown analytically. Here, therefore, we get two systems resulting from the adsorption of electrolytes by the same adsorbent one of which is positively charged and the other negatively charged, *i.e.*, the primarily adsorbed ion is a cation in the one case and an anion in the other case.

The two systems may be represented as follows :—



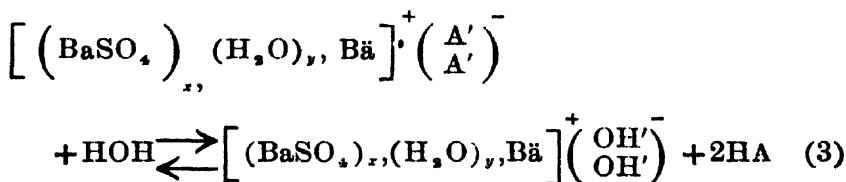
and



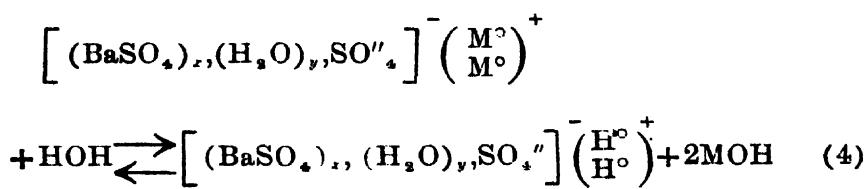
Systems III and IV have easily replaceable anions and cations respectively as these ions constitute the mobile layer of ions. On treatment with neutral salts, the anions will be replaced in system III and the cations in system IV. This has been observed to be the case. It must however be stated, as has already been pointed out, that the adsorbed electrolyte comes out in traces on washing

with fresh quantities of water or electrolyte, which is to be expected as there is an equilibrium between the adsorbed quantity and the concentration of the solute in solution and completely irreversible adsorption is a theoretical limiting case.

(4) From our point of view the following reactions are possible :—



and



The actual demonstration of the formation of both acid and alkali with the same adsorbent is rather difficult. The amount of the acid or alkali liberated depends on the total amount of the cation or anion primarily adsorbed and on the relative adsorbabilities of the hydrogen ion and the cation in one case, and of the hydroxyl ion and the anion in the other case. It has to be remembered that the replacement of the cation or the anion by hydrogen or hydroxyl ions respectively also depend on the concentration of the latter ions in pure water which is very small. Moreover, there is always the probability of the adsorbed electrolyte being removed on long continued washing, which has therefore to be avoided.

We have, however, been able to demonstrate the formation of acid and alkali with barium sulphate under the following conditions. If an amount of potassium sulphate be mixed with less than equivalent quantity of barium chloride the medium develops an alkaline reaction up to

$\rho_{\text{H}} = 11$; on the other hand with excess of barium chloride it develops an acid reaction of $\rho_{\text{H}} = 5$. The alkalinity and the acidity are also observed with barium nitrate and sulphate of the alkali metals. The conditions appear to be very favourable in this instance for the precipitation takes place in a medium containing the ions which are adsorbed and for the reason that the adsorption of the constituent ion is generally stronger than that of the other ions. Besides the adsorbed electrolytes are not removed as the experiment does not involve any washing.

It has been remarked before that lead and silver salts do not adsorb electrolytes to the same extent as barium sulphate does and this is probably responsible for our failure to obtain similar results with these salts. Our method of procedure precludes the observation of slight changes in the reaction of the medium. Further experiments on these lines are in progress.

D. Adsorption of Water and its Constituent Ions in their Relation to Hydrolytic Adsorption.

It has been stated before that the adsorbent need not be polar in character. We started with the substance BA because of the known capacity of such substances to adsorb electrolytes and in order to show that under certain conditions both acids and alkalis may be expected to be liberated from the interaction between water and the same insoluble salt containing adsorbed electrolytes.

We shall now consider the case where the adsorbent has a strong capacity to 'primarily' adsorb either hydrogen or hydroxyl ions, or both.

(1) Primary Adsorption of Hydroxyl Ions.'

'The system has an acidic character.'

We shall assume the system to be such that it can adsorb hydroxyl ions to a much greater extent than it can

adsorb hydrogen ions. Such a substance will have easily replaceable hydrogen ions in the mobile sheet and will act like an acid with the following characteristics, which differentiate it from ordinary acids.

(i) The substance will have a negative charge in contact with water, because of the adsorption of hydroxyl ions.

(ii) The adsorption of hydroxyl ions will evidently depend on their concentration in the solution and more will be adsorbed from an alkaline solution than from water unless the adsorption is so strong that the surface is saturated at the low hydroxyl ion concentration of pure water. The probability of such a state of affairs is remote. The substance will therefore adsorb alkalis in equivalent quantities so long as the activity of the hydroxyl ions is constant and the cation is not primarily adsorbed.

(iii) The negative charge will therefore increase on the addition of alkali from the greater adsorption of hydroxyl ions. Of course, at high concentrations of the alkali, the charge may decrease when the electrical adsorption of the cation predominates.

(iv) *The amount of replaceable hydrogen ions per gram adsorbent* is evidently constant for a given sample of the adsorbent so long as the concentration of hydroxyl ions in the solution correspond to that of neutral water and the solution does not contain acids with adsorbable anions or neutral salts with adsorbable cations, which can displace the primarily adsorbed hydroxyl ions.

In the case where acids only are present in the solution the total amount of anions adsorbed (hydroxyl and other anions) will determine the total amount of replaceable hydrogen ions, i.e., the maximum amount which is theoretically replaceable.

(v) If anions only are adsorbed then for the general case *the total amount of replaceable cations* (including hydrogen

ions), is determined by the total amount of anions (including hydroxyl ions) 'primarily' adsorbed.

(vi) The 'saturation capacity' of the surface with reference to cations (including hydrogen ion and bases) will depend on the amount of anions that can be adsorbed.

If we consider as Langmuir has suggested, that the number of places in the surface, where the anions are adsorbed, are determined by chemical valence, then the maximum amounts of different anions necessary to saturate the surface will follow a 'simple numerical ratio. The amount actually adsorbed will however depend on the composition of the solution.

The relationships will be simpler when the adsorbent has the strongest affinity for hydroxyl ions so that other anions are primarily adsorbed to a very small extent. It is also assumed that cation are not primarily adsorbed. The maximum amount of replaceable hydrogen ions is determined by the amount of hydroxyl ions adsorbed which is a constant quantity so long as the activity of the hydroxyl ions in the solution remains constant and the adsorption of the other anions does not change their number. The stoichiometric ratio of the amount of replaceable hydrogen ions to the number of gram molecules of the adsorbent, will depend on the specific surface and the capacity of the adsorbent to adsorb per unit surface.

(vii) On the addition of an acid the negative charge will decrease and there will be no reversal of charge unless there is also a "fixed" layer of primarily adsorbed molecules of water, provided that the surface cannot primarily adsorb hydrogen ions.

(viii) The adsorption of cations from salt solutions will not be equivalent to that of anions (excepting the case of alkalis) as there is always a replacement of the hydrogen ions by the cations.

In other respects the system will behave like the system BA with adsorbed acids.

(2) *Primary Adsorption of Hydrogen Ions.*

The system has a basic character.

The parallel case of a strong primary adsorption of hydrogen ions needs no further discussion. We might just mention that the surface will be charged positively in contact with water, will liberate alkalis in contact with 'neutral' salt solutions. The adsorption of the anion will be greater than that of the cation, the positive charge will increase in presence of acids and will diminish in contact with alkalis.

(3) *Primary Adsorption of Water Molecules.*

The system has an amphoteric character.

In the introductory portion of this paper it has been pointed out that hydrolytic adsorption can only result from a displacement (direct or indirect as shown below) of adsorbed hydrogen or hydroxyl ions by a cation or an anion respectively. In the preceding pages it has been stated that these displaced hydrogen ions or hydroxyl ions can come either from adsorbed acids or alkalis respectively or from the constituent ions of water. *We have so far associated the case of replacement of hydrogen or hydroxyl ions by 'neutral' salt solutions with their presence in the sheet of mobile ions of the double layer as electro-osmotic or allied measurements.* This view assumes that the surface carries an electric charge opposite in sign to that of the replaceable ion (hydrogen or hydroxyl) due to the primary adsorption of ions of one kind in excess. For the sake of simplicity we have so long considered that ions of one sign only are primarily adsorbed.

A theoretically important case which has not been considered so far is the rôle of the layer of primarily adsorbed molecules of water. From the point of view suggested in this and previous papers a 'primarily' adsorbed layer will act as a 'solid' layer (*cf. Phil. Mag., loc. cit.*, 332). It was suggested that such a system has in a sense amphoteric properties as the surface can neutralise or combine with hydrogen and hydroxyl ions in solution. The surface may acquire a positive charge in acid solutions and a negative charge in alkaline solutions. The conditions for such behaviour have been discussed in detail in the paper referred to above. These properties have been attributed to the dissociations of the 'primarily' adsorbed (solid layer) molecules of water. The case where the surface adsorbs primarily hydroxyl ions in addition to water molecules has also been discussed. *In general, however, such a surface will have a primarily adsorbed layer of neutral molecules of water, hydrogen and hydroxyl ions in equal number formed by the dissociation of small number of these molecules, and it may have in addition an excess of either hydrogen or hydroxyl ions, as the result of primary adsorption.* Their relative numbers will depend on the nature of the substance. *The system will have an acidic character when an excess of hydroxyl ions is primarily adsorbed and in suitable cases the number of hydrogen ions may be quite small compared to that of hydroxyl ions.* Similarly a system will have a 'basic' character when an excess of hydrogen ions is primarily adsorbed and a markedly amphoteric character when they are present in sufficient but equal amounts. Electro-osmotic and allied experiments give an idea of the net excess in charge and throw no light on the amount of each ion present in the primarily adsorbed layer.

The question now arises [Are these ions in the 'solid,' i.e., the primarily adsorbed layer displaceable by

other ions?" *A priori* there is no reason why they will not be so replaceable. Such a replacement is however distinct from exchange of ions of the same sign between those present in the mobile sheet of the double layer and those in the solution. Such exchanges are wholly electrical in nature and has very little to do with the chemical nature of the cations. The mobility, the charge and the adsorbability as defined in a previous paper (*Far. Soc. Disc., The Physics and Chemistry of Colloids*, loc. cit., p. 105) determine the capacity of the cations in the solution to replace those in the mobile sheet.

When the displacing ion is a cation the following possibilities arise :—(1) The cation can displace the hydrogen or hydroxyl ions ; or, (2) can take the place of neutral molecule of water ; or, (3) be adsorbed independently and directly without displacement. One or more of these possibilities may also occur simultaneously.

Displacement of Hydroxyl Ions from the Primary Layer.

(a) A replacement of a hydroxyl ion by a primarily adsorbed anion will not alter the charge of the surface unless there is a simultaneous independent adsorption of the anion. It will result in hydrolysis and alkali will be liberated and the acid will remain in the surface.

(b) A mere replacement of the hydroxyl ion by a 'primarily' adsorbed cation will not result in hydrolysis, for, to ensure the electrical neutrality of the double layer as a whole, the displaced hydroxyl ions must remain in the mobile sheet. If however the anion of the salt is present in sufficient concentration it may displace the hydroxyl ions from the mobile sheet, and alkali will be liberated. The surface will show a marked increase in the positive charge. One univalent cation so adsorbed will augment the positive electrical charge of the surface by two units due to the simultaneous displacement of the hydroxyl ions. On

the other hand if the surface had initially an excess of hydroxyl ions adsorbed (*i.e.*, if it has a marked negative charge in contact with pure water), the liberated hydroxyl ions will combine with hydrogen ions in the mobile sheet to restore the equilibrium between the two ions in these regions. Alkalies can only be liberated when the displaced hydroxyl ions are greater in amount than the hydrogen ions in the second sheet.

Displacement of Hydrogen Ions from the Primary Layer.

Parallel conclusions are to be drawn regarding the displacement of hydrogen or hydroxyl ions by anions.

Electrical Neutralisation of the Hydrogen or Hydroxyl Ions in the Primary Layer.

Another type of reaction that is theoretically possible from our point of view is that between the hydrogen and hydroxyl ions, formed from the dissociation of water molecules in the primarily adsorbed layer and the oppositely charged ions in the solution. The power of the hydrogen or hydroxyl ions to impart a positive or negative charge respectively to a surface, has been explained on the basis of interaction between hydrogen or hydroxyl ions in the surface and hydroxyl and hydrogen ions respectively in the solution. In this case the electrical neutralisation of opposite charges coincide also with the formation of undissociated molecules of water. One might also imagine a neutralisation of the electrical charges of the hydrogen or hydroxyl ions on the surface (resulting from the dissociation of the fixed layer of water molecules) and an oppositely charged ion in solution. The process is essentially a type of "electrical adsorption." This type of interaction would lead to different conclusions from the foregoing. *No alkalis can be liberated by the interaction between the surface and a cation and no acids can be*

liberated by interaction between the surface and an anion as oppositely charged ions are held together in the surface. The liberation of hydrogen ions by cations is only possible if we further assume that the force restraining the partner hydrogen ion of the neutralised hydroxyl ion is electrical in nature and as soon as the cation neutralises the charge of the hydroxyl ions the hydrogen ions become free to move out into the solution. The change in electrical charge will be slight or nil. Similarly an anion can only liberate alkalis.

In the foregoing we have pointed out several theoretically possible types of interaction between adsorbed water molecules, its constituent ions and ions in the solution, which can result in the liberation of acids or alkalis. We have also shown that a simultaneous measurement of the electrical condition of the surface, a study of the case with which different cations and anions liberate acids or alkalis, as also a study as to whether suitable cations or anions can liberate both alkalis and acids are necessary before we can form a definite picture of the nature of the interaction between the ions in the surface and those in the solution. Investigations from this point of view have not been attempted previously and hence in the few instances where experiments on hydrolytic adsorption have been carried out, it is difficult to draw a definite conclusion as to the type of the interaction. However, during the last few years a number of interesting investigations have been carried out which serve to illustrate our point of view.

(4). *Hydrated Silica as a Substance which has a strong Capacity to Adsorb Hydroxyl Ions and to a less extent other Anions.*

The nature of the interaction between silica and neutral salts is of considerable interest in agricultural

chemistry and has been the subject of controversy (Joseph and Hancock, *J. Chem. Soc.*, 1923, 123, 2022).

We shall briefly state here the experimental evidence that has been obtained in collaboration with Messrs. Kamala Charan Bhattacharya, Bhivas Chandra Ghosh and K. Krishna Murti. As the purity of the samples we have used has been questioned (Joseph and Hancock, *loc. cit.*) it is desirable to state that we have used hydrated silica obtained from the hydrolysis of doubly distilled silicon tetrachloride in vessels of fused transparent silica. Transparent silica vessels have been used as a rule. The hydrated silica contains traces of chlorine and excluding water contain 99.99% of silicon dioxide. The water content varied from about 90% to 50% of the total weight of the substance.

(1) Hydrated silica has a marked negative charge in contact with pure water, no matter how long the substance is washed with water.

(2) On the addition of acids (HCl, HNO₃) the negative charge decreases (*cf. Nature*, December 2, 1924). No reversal of the charge has been observed (*cf. Phil. Mag.*, *loc. cit.*, 330).

(3) In contact with solutions of neutral salts (NaCl, KCl, BaCl₂, RbNO₃, KNO₃, LiCl, LiNO₃) at low concentrations there is an increase in the negative charge, which, as is to be expected, is most marked in the case of lithium chloride, and the order of the cations arranged according to their power to decrease the negative charge is as follows :—H>Ba>Rb>K>Na>Li. The salts of hydrogen and barium mentioned above show no increase in negative charge. Using equivalent concentration of potassium salts it was found that the negative charge of the surface is increased by anions in the following order : oxalate>sulphate>chloride>bromide>nitrate.

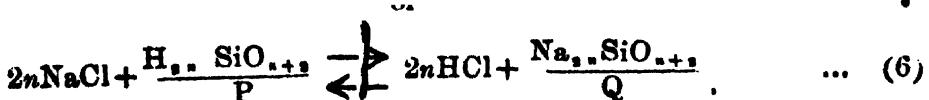
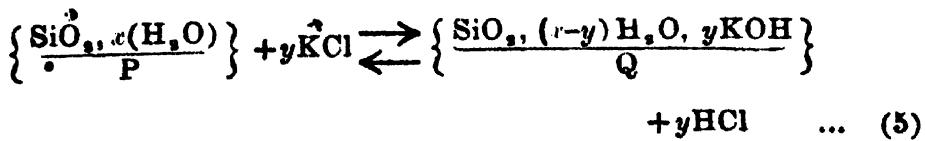
The increase in the negative charge shows definitely the 'primary' adsorption of these anions.

(4) Even in contact with very dilute solutions of alkalis the negative charge increased markedly and the increase is much greater than in the case of other salts of the same alkali metal cation (similar observations have also been made by others).

(5) Fourteen gms. of hydrated silica containing 11.2 gms. of water and 2.8 grams of silicon dioxide were kept in contact with 100 c.c. of saturated solution of potassium chloride for twenty-four hours. As much of the salt solution was decanted off, as could be separated without removing any silica and the volume and p_H of the extract was determined. A fresh volume of saturated potassium chloride was then added and after a contact of twenty-four hours or so the p_H and the volume of the decanted liquid were again determined. This process was repeated till the p_H of the extract became equivalent to that of the potassium chloride solution used. *In this manner it is possible to determine the total amount of replaceable hydrogen ions.* The hydrated silica contain 13.3 gram mols. of water per gram molecule of silicon dioxide and of these 13.3 gram mols. of water 3.5×10^{-4} gram atom of hydrogen ions is replaceable by potassium.

It will be seen that there is no simple stoichiometric relation between the amount of replaceable hydrogen ions and the number of gm. mols. of SiO_2 .

(6) If the reaction is really to be represented as follows :



(cf. Mellor, *Quantitative Inorganic Analysis*, London, 1913, p. 172, also Joseph, *loc. cit.*) one would expect that so long as the two solid phases *P* and *Q* co-exist the equilibrium concentration of the hydrogen ions would be determined by the concentration of potassium chloride used and would be constant when the latter remains constant. It is found, however, that as the washing continues the acidity of the extract falls steadily. It might be argued that equilibrium has not been attained and that as more of the insoluble acid *P* is transformed into the insoluble salt *Q*, it requires a much larger time to attain the equilibrium concentration. But this is not so, because if the time of contact is increased and the contents are shaken at intervals a maximum acidity is obtained which does not change any further with time.

(7) The increase in the negative charge showing the primary adsorption of anions leads us to expect the adsorption of acids (and salts). Ten grams of carefully washed hydrated silica are transferred to a Gooch crucible made of transparent fused silica without any asbestos or porcelain parts. If now 10 c.c. of an acid solution (HCl) of $p_H = 3.4$ are filtered through it the p_H of the extract rises to 4.6 showing that as much as 90% of the acid has been adsorbed. Other experiments have shown a change in p_H as large as from 3.2 to 5.0. Blank experiments using water instead of acid show no change in p_H . Also if no hydrated silica be present there is no change in p_H of the acid showing that the change in p_H is not due to any spurious effect. Further the extracted acid does not show the presence of ammonia. Neither can the water present in silica account for the diminution in concentration.

The amount of acid taken up is equal to 2.7×10^{-4} gram atoms of hydrogen ions per gm. mole of silicon dioxide.

(8) That silica can adsorb acids can also be shown directly in the following manner. Ten gms. of hydrated silica is shaken with 5 c. c. of normal oxalic acid and left in contact for a few hours. The silica is then washed with pure water till the water obtained after twelve hours' contact fails to decolourise 3 drops of an acid solution of $N/100$ permanganate when heated to about 60° for a quarter of an hour. The silica, however, decolourised 1.4 c. c. or about 40 drops of $N/100$ permanganate solution. This observation has been repeatedly confirmed.

The amount thus adsorbed works out to be 4.2×10^{-4} gram atoms of hydrogen per gm. molecule of SiO_2 .

It will be seen that the amounts given under (5), (7) and (8), ($3 \times 5 \times 10$, 2.7×10^{-4} , 4.2×10^{-4} gram atoms of hydrogen ions respectively per gram mol. of silicon dioxide) are comparable quantities. These quantities also illustrate the smallness of the amounts primarily adsorbed.

(5) Experiments with Hydrated Manganese Dioxide.

Hydrated silica is not the only substance which behaves in the above manner. Hydrated manganese dioxide prepared by Volhard's method has similar characteristics. As full experimental details and discussions will be published in a separate paper, we shall briefly relate an aspect of the experimental results which will illustrate the advantage of our point of view over the usual chemical one. It has already been stated that if the chemical point of view be correct there ought to a simple relation between the concentration (or activity) of the cation of the neutral salt and that of the hydrogen ions in the solution. We have found that this is not the case either with hydrated silica or with hydrated manganese dioxide. The concentration of the liberated hydrogen ions rises much more

slowly than that of the salt and reaches a maximum value. If we compare the influence of different cations, we find from the following table that at low concentrations the p_H of the liberated hydrogen ions increases in the following order: $Ba > K > Na > Li$. From the chemical point of view in the presence of the two insoluble phases P and Q the higher concentration (or activity) of the hydrogen ions is to be referred to the smaller solubility of the corresponding salt Q and the solubility must be assumed to increase in the order: $Ba < K < Na < Li$. As pointed out in a previous paper this order is met with in a large number of cases and for substances which are of widely different chemical composition (*vide Phil. Mag., loc. cit.*, pp. 339, 340, 343), and it is rather unusual that the solubilities will always be related in the above manner. The data shows moreover, that as the concentration of the cation rises the equilibrium hydrogen ion concentration rapidly tends to a constant value which is nearly the same for all the alkali metal cations. Besides the chemical point of view does not account for the electro-osmotic data. On the other hand the point of view advanced here gives a consistent explanation of these facts and in fact can predict a number of relationships.

The amount of liberated acid depends on the capacity of the cation to displace the hydrogen ions from the double layer. The concentration of the latter depends on the ratio of the two ions, hydrogen and the cation in the double layer and is determined by the electrical adsorbability of the cations. The electrical adsorbability of the cation also determines its effect on the negative

* The maximum hydrogen ion concentration does not represent the liberation of the total amount of replaceable hydrogen ions as fresh quantities of acid are set free on adding a fresh quantity of the salt solution to the solid residue. The maximum acid concentration, therefore, cannot represent a complete conversion of P into Q .

charge of the surface and therefore the same order ought to be observed in both cases. This fact is brought out in Table I.

TABLE I.

Rate of Electro-osmotic Flow.

pH Values.

Concentra-tion of electrolytes.	KCl	NaCl	LiCl	BaCl ₂	Concentra-tions.	KCl	NaCl	LiCl	BaCl ₂
0	9.8	9.8	9.8	9.8	N	2.16	2.15	2.17	...
N/5000	5.4	N/5	2.28	2.37
N/3000	7.4	16	17.7	...	N/10	2.34	2.47	2.67	2.09
N/1000	5.4	16.3	16.6	+8.0	N/100	2.99	2.76	3.00	2.21
N/500	3.3	13.1	14.3	+13.0	N/200	2.40
N/250	2.0	11.7	13.4	+16.7	0	5.8	5.8	5.8	5.8
N/125	+14.5					

The fact that at higher cation concentrations the hydrogen ion concentration tends to a limiting value can also be accounted for. The adsorbability of the cation, the variation in the electrical charge of the surface with its concentration, and the amount and concentration of liberated hydrogen ions are closely related to one another. The total amount of replaceable hydrogen ions, the composition of the primarily adsorbed layer and of the mobile layer of ions are to be taken into consideration, in order to elucidate the relationships between the electrical charge

* The electro-osmotic data given above represents the distance moved by the air bubble in 3 minutes. With BaCl₂, reversal of charge was obtained at N/1000 for the sample which has used in the electro-osmotic experiments. This sample was much coarser grained and more thoroughly washed than the one used for measurement of pH. The sample of MnO₂ used for pH measurement showed a reversal of charge with BaCl₂ between N/200 and N/66.6. The pH of water kept in contact with MnO₂ for 24 hrs. is 5.8. E. M. F. measurements have been made in each case to check the values obtained from the use of indicators. The two are in satisfactory agreement.

and the concentrations of liberated hydrogen ions. These relationships have sufficiently brought out the unsuitability of the usual chemical point of view. As it will be necessary to enter too much into detail the consideration of these interesting relationships will be taken up in the paper dealing with hydrated manganese dioxide.

(6) *Experiments of Bartell and Miller on Active Charcoal.*

Bartell and Miller (*J. Amer. Chem. Soc.*, 1922, 44, 1866; *ibid.*, 1923, 45, 1106; 1924, 46, 1150; *J. Phys. Chem.*, 1924, 28, 992), have clearly demonstrated hydrolytic adsorption by ash-free active charcoal from sugar. Their experiments also prove the existence of the type of reactions postulated under D. The ease with which simple electrolytes like solutions of potassium chloride or potassium nitrate can liberate alkalis leads one to expect that hydroxyl ions are present in the mobile sheet of the double layer. There are, however, no measurements of the electrical charge and of the total amount of replaceable alkali and in the absence of these data, it is not possible to give a definite account of the changes taking place in the surface layer. Such measurements are more necessary because Bartell and Miller have used not only simple electrolytes like potassium chloride but have also used electrolytes containing complex cations and anions and chemical affinity between the surface atoms and the ions in the solution will have to be considered. The correlation of the electrical with the chemical data is of great interest. The data of Bartell and Miller, though incomplete in the above sense, points strongly to the capacity of their charcoal to adsorb preferentially hydrogen ions and that the surface has probably a weak or very little power to adsorb hydroxyl ions. The ease with which alkalis are liberated (in fact all ordinary salts excepting that of

mercury and silver liberate alkalis only) and the fact that alkalis are not at all adsorbed support this statement (*vide Miller, J. Amer. Chem. Soc., 45, loc. cit.*). The liberation of acids by silver and mercury salts are in agreement with the strong primary adsorption of these ions as shown by their capacity to impart a positive charge to the surface (*cf. Mukherjee and Roy, loc. cit.*). Their charcoal would probably show a positive charge in contact with pure water and would show only a small, if at all any, negative charge in the presence of alkalis. Acids are likely to increase the positive charge, a detailed consideration of the nature of the changes in the surface layer must be postponed till the necessary data have been obtained.

In the foregoing we have outlined some simpler types of reactions to illustrate our theory. More complicated cases will be considered in the papers to follow.

We have so far considered reactions concerning the primarily adsorbed layer and ions in the mobile sheet of the double layer. We shall now consider more fully the rôle of the 'adsorbed' water in the analytical estimation of the amount of 'primary' adsorption and in the retention of a solute by an adsorbent as these questions have a very important bearing on subsequent papers.

E. *Hydration of the Substance and its Relation to Adsorption.*

The primarily adsorbed layer is probably one molecule thick and does not extend much beyond it. The molecules in this layer are held by chemical affinity of the atoms on the surface of the adsorbent and act as a 'solid' layer. Ions in the mobile layer are also not wholly free to move in the sense that there must be always an amount of ions equivalent to the free and fixed charge on the surface.

There is, however, evidence to show that the 'adsorbed' layer of molecules of water, which hydrate the surface,

is not a unimolecular layer but rather forms a layer several molecules in depth. Thus hydrated silica containing as much as 80% of water behaves to most purposes as a solid. The number of gm. molecules of water per gram molecule of silicon dioxide works out at about 13 mols of water to 1 mol of silicon dioxide. It is evident that the hydration layer must be several molecules deep.

The strength with which the successive layers of water molecules are held in the poly-molecular hydration layer will fall off rapidly, as the distance from the adsorbing surface increases. A '*fully hydrated surface*' can be defined as one where the poly-molecular layer is sufficiently deep so that the outermost layer of water molecules will show the same vapour pressure as pure water at that temperature. As the successive layer of water molecules *counting from the outermost layer evaporates*, the vapour pressure will diminish because the successive layer of molecules are adsorbed with increasing intensity. It is well known that the presence of water vapour falls off rapidly with the percentage of hydration. The layer immediately in contact with the surface is held by chemical affinity and there is a marked drop in the intensity of the forces with which the following layers are held by the surface. Thus we would distinguish between the 'primarily' adsorbed layer and the poly-molecular hydration layer. Different types of forces, as distinct from what we ordinarily refer to as chemical valence and analogous to inter-molecular attraction as represented by the a/v^2 term in van der Waals's equation, or forces akin to those causing the hydration of ions are probably responsible for the formation of this layer. The water molecules whose dissociation has been discussed are assumed to be in the 'primarily' adsorbed layer. ¶

*Adsorption of Water and Analytical Estimation
of Adsorption.*

The importance of the adsorption of water in analytical estimation of adsorption has been emphasised by Bancroft and Williams and more recently by Ostwald and Izagguire (*Koll. Zeit.*, 1919, 30, 279). Bancroft pointed out that the water-content of the adsorbent is to be taken into consideration in calculating the amount adsorbed (*cf.* Weiser and Sherrick, *J. Phys. Chem.*, 1919, 23, 205). The effect of adsorbed water is considered to be merely to dilute the solution in virtue of the penetration of the solute molecules into the 'hydration' layer. Apparently the assumption is being made that the distribution coefficients of the solute between the solution and the adsorbed layer of water is unity. The hydration layer does not behave exactly as a 'solid' layer as salts are not soluble in ice; that is, in the hydration layer probably there is no regular lattice arrangement as in solid ice. •

On the other hand it is not possible to look upon the effect as mere dilution with water. There is always a time factor involved in the diffusion of the solute from the 'hydration' layer into the bulk of the liquid and from experiments on the time necessary to wash out the solute it appears to us that a simple mechanical mixing of the water in the hydration layer with the solution during washing, cannot account for the time taken to remove the solute from the hydration layer. Very accurate measurements of the change in concentration of a solution in contact with a hydrated adsorbent will enable us to determine the relationship between the concentration in the hydration layer and that in the bulk of the solution. We have already stated that small but demonstrable quantities of acids are adsorbed by hydrated silica and hydrated manganese dioxide. The partition ratio cannot therefore

be unity though we have found at higher concentrations the small amount actually adsorbed does not materially alter the total concentration and a partition coefficient equal to unity is observed. Moreover, the internal pressure of the water in the hydration layer is certainly different from that inside the pure liquid, and it is to be expected, that this would change the free energy and the partition coefficient would be different from unity though the magnitude of the effect as we have seen is probably very small. The well-known suggestion of Lagergren (*loc. cit.*) and also the considerations put forth by Williams (*cf. Phil. Mag.*, *loc. cit.*, pp. 323-24) also lead us to expect a difference in concentration and an adsorption effect from the existence of the hydration layer and more exact and detailed experiments are desirable.

We have entered into a detailed consideration of the effect of the water of hydration with a view to show that the estimation of the amount of primary adsorption by direct analytical measurements is beset with considerable difficulties and to show that the effect of the water of hydration is not simply one of dilution. We are of opinion that the adsorbed amount should be defined as the total amount taken up by the adsorbent including that by the water of hydration. This method of representation is more advantageous as emphasising the fact that a solid can take up a solute which is not soluble in it, in virtue of its water of hydration. Attention is not directed to this fact if the results are expressed in the usual way. Ostwald and Izagguire (*loc. cit.*) state 'Es werden nicht "gelöste Stoffe," es werden vielmehr "Lösungen" selbst adsorbiert. Es ist demnach auch sprechlich, schärfen nicht von Adsorptionen, "in" oder "aus" Lösungen sondern von Adsorptionen "von" Lösungen zu sprechen.'

'The retention of electrolytes (including acids) in the hydration layer is of considerable importance in

agricultural chemistry. There is always a time factor depending on the rate of diffusion from the surface layers which makes the removal of the solute by drainage water slow and difficult. Also the difference between adsorption as usually determined by analysis and the adsorption we are considering just now, is none of degree so far as the rate of removal by washing is concerned. In the case of the 'primarily' adsorbed molecules all are not free to diffuse but in the latter case the freedom of the solute molecules to diffuse out of the hydration layer is almost equal to that of the molecule in the bulk of the liquid. On the other hand the total amount of solute in the hydration layer is much greater. So that in considering the retention of the solute, say, by soil particles, the effect of the hydration is not less important than that represented by the amount adsorbed after correcting for the hydration. The writer therefore suggests that the adsorption ought to be calculated in terms of the total change in concentration of the solution brought in contact with the solid adsorbent—irrespective of the water content of the latter, and that the facts can be better represented by simultaneously mentioning the 'hydration' of the solid phase.

(F) *Base-Exchange in Soils.*

The application of the considerations set forth above to the problem of exchange of bases in soil is evident, in so far as the exchange is to be attributed to an interaction between the ions in the solution with those in the double layer. The same considerations regarding the 'saturation capacity' of the surface with respect to different anions, the electrical and chemical adsorbability of various cations and the concentrations of the different ions in the solutions are applicable to this case. It is our

intention to deal with the exchange of bases in soils from our point of view in one of the papers of this series.

Conclusion and Summary.

In conclusion we would like to emphasize that we have only considered certain simple theoretically possible cases and that more complicated changes where chemical affinity plays a very important part and which are to be met with quite frequently, have been left out of consideration.

In this paper, the view advanced by the author regarding the distribution of ions in the 'Helmholtz' electrical double layer have been further developed to account for hydrolytic adsorption. The different types of reaction, which from this point of view can liberate acids or alkalis from neutral salt solutions, have been described and a brief summary of the experimental results to be communicated in the following papers, has been given in support.

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Hetero-Ring Formations with Thio-Carbohydrazide

Part II

Condensations with Diketones and Aldehydes

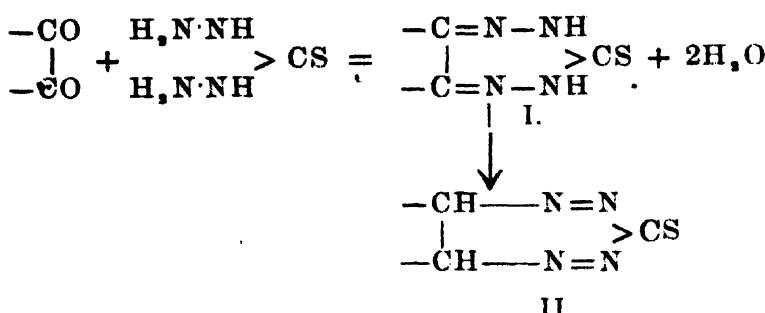
BY

PRAPHULLA CHANDRA GUHA AND SATIS CHANDRA DEY.

In a previous communication (this *Journal*, 1924, 1, 141) a number of cases of hetero-ring formations with thiocarbohydrazide has been described. The present investigation was undertaken with the object of making a comparative study of the behaviour of *ortho*-diketones with hydrazine, urea, semicarbazide on the one hand and with thiocarbohydrazide on the other. Curtius and his collaborators (*J. pr. Chem.*, 44, 169, 188; *Ber.*, 22, 2161) obtained different types of compounds from varying quantities of hydrazine hydrate and several *ortho*-diketones. Interesting bridged-ring compounds have been obtained from glyoxal and some *ortho*-diketones by the action of carbamide by Bottinger (*Ber.*, 10, 1923); Schiff (*Annalen*, 189, 15), Franchimont and Klobie (*R.* 7, 251), Angeli (*Gazetta*, 19, 563; *Ber.*, 24, 606), Anschütz and Geldermann (*Annalen*, 261, 129). Again Thiele and Stanger obtained a triazine compound from benzil and thiosemicarbazide and later on, Bromberg (*Ber.*, 30, 132) obtained an additive compound and a semicarbazone with alloxan and its dimethyl derivative. Schmidt and Sauer (*Ber.*, 44, 3250), Schmidt, Schainer and Glatz (*Ber.*, 44, 276) obtained a semicarbazone

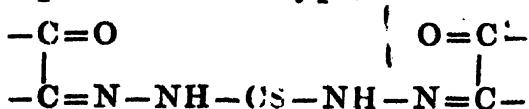
from phenanthraquinone and a triazine compound from its monoxime.

One molecule of thiocarbohydrazide reacts with one of benzil, acenaphthaquinone, camphorquinone and alloxan with the formation of compounds which may be regarded as closed ring thiocarbohydrazones (I).



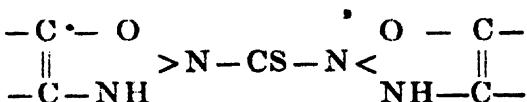
Now it is a well-known fact that when an atomic grouping -NH-CS-NH- is present in a compound, especially when it forms part of a ring, the compound, by virtue of the presence of the potential mercaptanic group, dissolves in alkalis and forms disulphides and thio-ethers. But it is curious to note that the supposed cyclic compounds so formed do not exhibit any mercaptanic properties, which precludes the possibility of the above atomic grouping being present and hence the present authors suggest the alternative constitution (II), which would result from the migration of two hydrogen atoms. Similar cases of migration resulting in the change of hydrazones into azo-compounds are well-known.

In the case of phenanthraquinone and isatin two molecules react with one molecule of thiocarbohydrazide yielding compounds of the type,

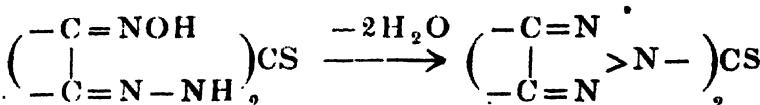


only one ketonic group of the diketones being reactive. The compounds so formed are also found to be insoluble

in alkalis. In order to account for a similar phenomenon, *viz.*, the insolubility of benzene-azo- β -naphthol or β -naphthaquinone phenylhydrazone in alkali, different non-hydroxylic formulae have been suggested by Liebermann (*Ber.*, 16, 2863), Zincke and Lawson (*Ber.*, 20, 2903) and Meldola (*Phil. Mag.*, 1888, 11, 411); and by analogy with the view of Liebermann the present authors assign to their compounds the modified formula,



The monoxime of isatin reacts with thiocarbohydrazide forming a normal thiocarbohydrazone of the oxime, which in its turn furnishes a thio-keto-bis-triazole compound when heated in a sealed tube with concentrated hydrochloric acid, thus :



Phenanthraquinone-monoxime gives the triazole compound at once and the intermediate oxime-thiocarbohydrazone is not isolated. The above type of bis-triazole compounds are insoluble in alkali and form black sulphide of mercury with mercuric oxide, showing respectively the absence of any mercaptanic group and the presence of the sulphur atom in the thio-ketonic form.

Thiocarbohydrazide yields compounds of the type $CS(NH:N=CRR')_2$ with aldehydes and ketones. Attempts to condense one molecule of the hydrazide with one of the aldehyde or ketone have been unsuccessful. Benzaldehyde, *m*-nitrobenzaldehyde, salicylaldehyde, cinnamic aldehyde, anisaldehyde, furfural, piperonal, acetone, methylethyl ketone, acetophenone, and benzophenone have been condensed with thiocarbohydrazide.

The thiocarbohydrazones of the aldehydes and ketones have been found to give rise to an interesting class of compounds with acid chlorides, esters of α -halogenated acids and α -halogenated ketones which in their turn are expected to form interesting fused-ring heterocyclic compounds with suitable reagents. The action of *o*-diketones on carbohydrazide and thiosemicarbazides is also under investigation and in a few cases, interesting results have already been obtained.

EXPERIMENTAL.

3-Thioketo-6:7-diphenyl-1:2:4:5-heptatetrazine.

A mixture of benzil (1 part), thiocarbohydrazide hydrochloride (1 part) and glacial acetic acid was heated under reflux. The reaction began at once as was indicated by the gradual disappearance of the hydrazide hydrochloride, which is insoluble in this solvent. On continued heating the solution became first yellow and then brown and after many hours deposited a small crop of light yellow crystals. This was filtered and washed with water and acetone. It melts at $118^\circ - 120^\circ$. The yield is extremely poor. (Found : N = 20.32. $C_{15}H_{12}N_4S$ requires N = 20.00 per cent.)

It is insoluble in water, acetone, benzene; very soluble in alcohol and pyridine from which it could not, however, be crystallised. It is insoluble in dilute mineral acids and caustic alkalis. The mother-liquor on dilution with water deposited a brown resinous mass which was extremely soluble in all organic solvents. An attempt to isolate a second product from this resinous mass was attended with failure.

3-Thioketo-acenaphtha-1:2:4:5-heptatetrazine.

A mixture of acenaphthaquinone (1 part) and thiocarbohydrazide hydrochloride (1 part) was heated with acetic acid under reflux for 2 to 3 hours. The solid mass so formed was separated by filtration from the mother-liquor while hot and washed with acetic acid and water. It was then purified by crystallisation either from boiling nitrobenzene or from pyridine. As obtained from these solvents it possesses a dark brown colour and melts at 253° . (Found : N = 22.41. $C_{13} H_8 N_4 S$ requires N = 22.22 per cent.)

It is insoluble in alcohol, acetone, benzene and acetic acid ; soluble in pyridine and nitrobenzene. It is insoluble in dilute mineral acids and caustic alkalis. Concentrated sulphuric acid dissolves it with a dark brown colour.

3-Thioketo-camphor-1:2:4:5-hepta-tetrazine.

A mixture of camphorquinone (1 part) and thiocarbohydrazide hydrochloride (1 part) was heated with glacial acetic acid under reflux for several hours. The solution became first yellow and then reddish-brown and after filtering and allowing to cool and stand, deposited a light yellow precipitate which was separated and crystallised from nitrobenzene. It was thus obtained as yellow needles which did not melt even at 290° . (Found : N = 23.82. $C_{11} H_{16} N_4 S$ requires N = 23.73 per cent.)

It is insoluble in acetone, benzene, and chloroform ; readily soluble in alcohol and fairly soluble in acetic acid or boiling nitrobenzene. It is insoluble in dilute mineral acids and caustic alkalis. Concentrated sulphuric acid dissolves it producing a yellow colouration.

3-Thioketo-allojan-1:2:4:5-hepta-tetrazine.

When a mixture of alloxan (1 part), thiocarbohydrazide hydrochloride (1 part) and glacial acetic acid was

heated under reflux there separated an orange coloured substance in the course of 4 to 5 minutes. The mixture was further heated for about half an hour and the solid mass was separated from the hot mother-liquor by suction. It was then washed with acetic acid and water and finally crystallised from pyridine in pale orange crystals which did not melt even at 295°. (Found: N = 39·69. C₅H₄O₂N₆S requires N = 39·62 per cent.)

It is insoluble in water, acetic acid, acetone, alcohol, nitrobenzene and benzene; readily soluble in hot pyridine. It is insoluble in dilute mineral acids and dissolves readily in caustic soda. Concentrated sulphuric acid dissolves it with a brown colour.

Di-phenanthraquinone-thiocarbohydrazone.

Thiocarbohydrazide hydrochloride (1 part) was mixed with phenanthraquinone (2 parts) dissolved in glacial acetic acid and heated under reflux when a reaction began at once and the solution turned red. Red crystals began to separate out after 2 to 3 minutes and for the completion of the reaction heating was continued for a further period of 15 to 20 mins. The red precipitate was boiled with acetic acid to remove excess of phenanthraquinone, and unchanged theocarbohydrazide hydrochloride was removed by washing with water. The hydrazone so obtained possesses a beautiful vermillion colour, and is sufficiently pure for analysis; it melts at 242°. (Found: N = 11·49. C₂₉H₁₈O₂N₄S requires N = 11·52 per cent.)

When the substance is crystallised from pyridine its colour becomes lighter. The needle-shaped crystals thus obtained contain one molecule of pyridine of crystallisation. (Found: N = 12·59. C₃₄H₂₃O₂N₄S requires N = 12·39 per cent.)

Di- β -naphthaquinone-thiocarbohydrazone.

A mixture of β -naphthaquinone (2 parts) and thiocarbohydrazide hydrochloride (1 part) was heated with acetic acid under reflux for about an hour and a half. The black solid mass thus formed was filtered off from the hot solution and was washed with water. It was then extracted with pyridine and the solution boiled with animal charcoal. The filtrate gave a grey-coloured flocculent amorphous precipitate on the addition of water. In order to purify it further, it was dissolved in boiling nitrobenzene from which a grey-coloured amorphous mass was obtained which did not melt even at 290°. (Found : N = 14.04 ; S = 7.85. $C_{21}H_{14}O_2N_4S$ requires N = 14.51 ; S = 8.29 per cent.)

It is insoluble in water, acetic acid, alcohol, acetone and benzene; readily soluble in pyridine and nitrobenzene: insoluble in dilute mineral acids and caustic alkalis and is charred by concentrated sulphuric acid.

Di-isatin-thiocarbohydrazone.

A mixture of isatin (2 parts) and thiocarbohydrazide hydrochloride (1 part) was heated in acetic acid for about half an hour when there separated a deep orange-coloured precipitate which was filtered off from the mother-liquor, washed successively with acetic acid and water and finally crystallised from boiling nitrobenzene in orange-coloured needles which melted with decomposition at 262°. (Found : N = 23.52. $C_{17}H_{12}O_2N_6S$ requires N = 23.07 per cent.)

It is insoluble in water, acetone, benzene, chloroform and acetic acid; almost insoluble in alcohol; readily soluble in pyridine and boiling nitrobenzene and insoluble in dilute mineral acids. It can be precipitated by hydrochloric acid from the red coloured solution which it forms with dilute caustic alkalis. It dissolves in concentrated sulphuric acid with a violet-red colour.

Thiocarbohydrazone of Diacetyl monoxime.

Diacetyl monoxime (2 parts), thiocarbohydrazide hydrochloride (1 part) and acetic acid were heated under reflux for about 5 to 6 hours, after which the filtered solution was allowed to stand over-night. As no solid separated out, the acetic acid solution was diluted with water when a grey coloured amorphous mass was precipitated. This was filtered and washed with water. In order to purify it further, a pyridine solution of this substance was boiled with animal charcoal and the filtered solution on dilution with water, deposited an amorphous precipitate which chars at 220° and then melts at 285° . It could not be crystallised from any organic solvent. (Found: N=31.11; S=12.02. $C_9H_{16}O_2N_6S$ requires N=30.88; S=11.76 per cent.)

It is insoluble in alcohol, acetone, benzene and chloroform; readily soluble in acetic acid and pyridine. It is insoluble in dilute mineral acids but dissolves in dilute caustic alkalis with the formation of a red coloured solution.

Thioketo-bis-dimethyl-triazole.

When the above oxime-hydrazone was heated with glacial acetic acid containing concentrated hydrochloric acid in a sealed tube at 100° for five to six hours, it was converted into an insoluble solid mass. This was filtered and washed with water till free from acids. It could not be crystallised from any organic solvent and it does not melt at 300° . (Found: N=35.82; S=13.28. $C_9H_{12}N_6S$ requires N=35.59; S=13.56 per cent.)

It is insoluble in most organic solvents; dilute mineral acids and caustic alkalis have no solvent action upon it.

Thioketo-bis-phenanthratriazole.

A mixture of phenanthraquinone monoxime (2 parts) and thiocarbohydrazide hydrochloride (1 part) was heated under reflux with acetic acid. The reaction began on gentle warming with the separation of a reddish brown crystalline mass. Heating was continued for about half an hour when the reaction came to an end. The precipitate was separated from the hot mother-liquor, washed repeatedly with hot acetic acid and then with water in order to free it from any unchanged reacting materials. It was crystallised from boiling nitrobenzene in needles melting at 230°. (Found : N=18·03. C₂₈H₁₆N₆S requires N=17·50 per cent.)

It is insoluble in alcohol, acetone, benzene, chloroform and acetic acid ; readily soluble in boiling nitrobenzene and pyridine ; insoluble in dilute mineral acids. It dissolves very sparingly in boiling dilute caustic soda with a pink colour. In concentrated sulphuric acid, it dissolves without charring with a brown colour.

Thiocarbohydrazone of Isatoxime.

Thiocarbohydrazide hydrochloride (1 part) was added to a solution of isatoxime (2 parts) in boiling glacial acetic acid. The solution soon turned red. The mixture was heated for about three hours for the completion of the reaction, filtered and allowed to stand over-night, when greenish yellow needles were deposited. These were separated from the mother-liquor by filtration and washed with water to remove the excess of hydrazide hydrochloride. For further purification it was crystallised from nitrobenzene in yellow needles which melt with decomposition at 228°. (Found : N=28·76. C₁₁H₁₄O₂N₆S requires N=28·43 per cent.)

It is insoluble in water, acetone and benzene; readily soluble in alcohol, acetic acid and nitrobenzene; insoluble in dilute mineral acids but readily soluble in dilute caustic soda with a red colouration from which it can be precipitated again by hydrochloric acid. It dissolves in concentrated sulphuric acid with a deep red colour.

Thioketo-bis-isatintriazole.

When the above oxime-hydrazone was heated with alcoholic hydrochloric acid in a sealed tube at 100° for several hours it was converted into an insoluble solid mass which was filtered off washed with alcohol to remove any unconverted oxime-hydrazone and finally crystallised from pyridine in yellow needles with a greenish tinge which do not melt at 290° . (Found : N = 31.58. $C_{17}H_{10}N_8S$ requires N = 31.28 per cent.)

It is insoluble in alcohol, acetone, benzene and chloroform; sparingly soluble in acetic acid; readily in pyridine and nitrobenzene. It is insoluble in dilute mineral acids, or alkalis. It dissolves in concentrated sulphuric acid with a red colour.

CONDENSATION WITH KETONES AND ALDEHYDES.

Dibenzylidene-thiocarbohydrazone.



To an aqueous solution of one gram of thiocarbohydrazide hydrochloride was added an alcoholic solution of two grams of benzaldehyde with frequent shaking. The reaction began at once with the separation of a slightly yellowish amorphous flocculent precipitate. This was filtered off, washed with alcohol and crystallised from boiling acetic acid in which the dibenzylidene compound is moderately soluble. It melts at 194° . (Found : S = 11.14. $C_{15}H_{14}N_4S$ requires S = 11.35 per cent.)

The dibenzylidene-thiocarbohydrazone is slightly soluble in cold, moderately soluble in hot alcohol; insoluble in ether and water. The alcoholic solution gives with alcoholic silver nitrate solution a yellow gelatinous precipitate.

Di-m-nitrobenzylidene-thiocarbohydrazone.

Thiocarbohydrazide (1 gm.) was dissolved in cold water containing a few drops of conc. hydrochloric acid and to the solution so obtained was added a hot alcoholic solution of *m*-nitrobenzaldehyde (1 gm.) with constant shaking. The reaction began with the evolution of heat and separation of a light yellow mass which was filtered off, washed with alcohol and then purified by boiling with alcohol. It was thus obtained as a light yellow powder of melting point 227°. (Found : N = 22.62. $C_{15}H_{12}O_4N_6S$ requires N = 22.58 per cent.). It is hardly soluble in ordinary organic solvents.

Di-cinnamylidene-thiocarbohydrazone.

Cinnamic aldehyde (0.8 gm.) was dissolved in alcohol and to this an aqueous solution of 1 gm. of the hydrazide hydrochloride was added gradually with frequent shaking. A yellow precipitate was formed at first but with the further addition of the aldehyde solution the whole was converted into an orange-coloured mass which solidified on standing for some time. This was filtered off and subjected to the action of steam to remove unchanged aldehyde. The residue after filtration was boiled twice with alcohol, which removed the greater portion of the tarry impurities and was finally crystallised from boiling nitrobenzene in yellow plates melting at 235° with decomposition. (Found : N = 16.68. $C_{16}H_{18}N_4S$ requires N = 16.76 per cent.) The yield of the pure compound was not good.

Di-cinnamylidene-thiocarbohydrazone is completely insoluble in water, ether, benzene and chloroform; very sparingly soluble in hot alcohol or acetone; readily soluble in boiling nitrobenzene from which it crystallised in yellow plates.

Di-o-hydroxybenzylidene-thiocarbohydrazone.

An alcoholic solution of salicylaldehyde (1 gm.) was added to the aqueous solution of thiocarbohydrazide hydrochloride (1 gm.). To avoid the formation of a resinous mass, it was found best to add the aldehyde solution drop by drop. The reaction began with the separation of a yellow precipitate; after the addition of the aldehyde solution was over, the mixture was allowed to stand. The precipitate was filtered off and crystallised from acetone in almost snow-white shining plates melting at 190° with decomposition. (Found: S = 10.31. $C_{15}H_{14}O_2N_4S$ requires S = 10.19 per cent.)

It is soluble in alcohol and acetone, insoluble in warm ether, benzene and chloroform.

Di-anisylidene-thiocarbohydrazone.

Anisaldehyde (1.3 gms.) dissolved in dilute alcohol was added to 1 gm. of thiocarbohydrazide dissolved in water containing a few drops of conc. hydrochloric acid. The mixture of the two reactants was thoroughly shaken. A white precipitate was formed mixed with a small quantity of a resinous product and some unconverted aldehyde which rendered the whole mass pasty. On scratching with a glass rod for some time, this was converted into a brittle mass, which, after filtration, was boiled for some time with ether and then crystallised from acetone. It melts at 158° . (Found: N = 16.22. $C_{17}H_{18}O_2N_4S$ requires N = 16.37 per cent.)

The dianisylidene compound is insoluble in water, ether and chloroform; sparingly soluble in boiling benzene from which it is precipitated in an amorphous condition. It can, however, be readily crystallised from a mixture of acetone and water in light-yellow plates.

Di-furfuryl-thiocarbohydrazone.

From a mixture of 1 gm. of thiocarbohydrazide hydrochloride and 1 gm. of furfural a dirty brown mass separated out mixed with some unconverted aldehyde. On allowing the mixture to stand for some time it solidified. The powdered mass was freed from volatile impurities by means of steam and was finally crystallised from acetic acid. It melts with decomposition at 250°. (Found : S=12·02. C₁₁H₁₀O₂N₄S requires S=12·21 per cent.) It is insoluble in water, ether and benzene; sparingly soluble in hot acetone but readily in hot alcohol from which it is obtained in globular aggregates. It can be crystallised from acetic acid in rectangular plates.

Di-piperonyl-thiocarbohydrazone.

To an aqueous solution of 1 gm. of the hydrazide hydrochloride was added about 1 gm. of piperonal. The mixture was then gently warmed on the water-bath and vigorously shaken when a yellow mass was obtained. Crystallised from acetone or acetic acid it melts at 195° with decomposition. (Found : N=15·10. C₁₇H₁₄O₄N₄S requires N=15·14 per cent.) It is insoluble in water, alcohol, benzene and chloroform moderately soluble in acetone from which it separates out in rectangular plates with a faint yellow tinge. It is obtained from boiling nitrobenzene in amorphous form and from boiling acetic acid in light yellow plates.

Di-acetone-thiocarbohydrazone.

An excess of acetone was added to 1 gm. of thiocarbohydrazide. In the cold no reaction took place but when the mixture was boiled under reflux, the hydrazide began to dissolve in acetone and within several hours, most of the hydrazide went into solution. The solution was cooled and freed from a small quantity of an undissolved residue by filtration and the filtrate concentrated. When water was added to the concentrated acetone solution a white precipitate was obtained and this, for further purification, was again dissolved in the minimum quantity of acetone and precipitated by water as crystals which melt with decomposition at 195°. (Found : S = 17·06. C₇H₁₄N₄S requires S = 17·20 per cent.)

Di-acetophenone-thiocarbohydrazone.

The mixture of the constituents in dilute alcoholic solution was shaken and finally heated on the water-bath for a few minutes. The filtered mass was treated with steam and the residue crystallised from alcohol in plates melting at 185°. (Found : N = 17·93. C₁₇H₁₈N₄S requires N = 18·06 per cent.)

Di-benzophenone-thiocarbohydrazone.

No reaction took place on warming the reactants in alcoholic solution on the water-bath. But as soon as some sodium acetate was added, the reaction commenced at once with the separation of a white solid mass. After allowing the mixture to stand for a few minutes, the precipitate was filtered off, washed with dilute alcohol and then crystallised either from absolute alcohol or from acetic acid. The crystals so obtained melt slowly at 223° with evolution of white fumes and on being rapidly heated it melts at 230° with decomposition.

(Found : N = 12.68. C₂₇H₂₂N₄S requires N = 12.9 per cent.) It is insoluble in water, benzene, ether, chloroform and nitrobenzene; very slightly soluble in cold alcohol and acetic acid, but moderately soluble in boiling alcohol and acetic acid.

Di-methylethylketone-thiocarbohydrazone.

Thiocarbohydrazide (1 gm.) was covered with excess of methylethylketone and the mixture was then heated under reflux till all the hydrazide was dissolved. The filtered solution was then concentrated when crystals of the hydrazone separated out. A further quantity was obtained by adding water to the mother-liquor. Crystallised from water the hydrazone softens at 215° and melts at 220° with decomposition. (Found : S = 14.86. C₉H₁₈N₄S requires S = 14.95 per cent.) It is insoluble in ether, chloroform, benzene and alcohol.

Our best thanks are due to Sir P. C. Ray and Dr. J. C. Ghosh for the kind interest they have taken during the course of the investigation.

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The Preparation of Methyl and Ethyl Iodides from the Corresponding Toluene Sulphonates

BY

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The preparation of methyl iodide from dimethyl sulphate is a well established method but suffers from the disadvantage that only one methyl group is converted to methyl iodide. It has been found that the dimethyl sulphate can be replaced by methyl toluene sulphonate with satisfactory results. Ethyl iodide can be prepared by a similar method.

EXPERIMENTAL

(1) *Methyl Iodide*.—42 gms. of potassium iodide were dissolved in 42 c.c. of water and 47 grams of methyl-*p*-toluene sulphonate added. The mixture was distilled from a sand-bath. The yield of dry, redistilled methyl iodide was 30 grams or 84·5%.

(2) *Ethyl Iodide*.—42 gms. of potassium iodide were dissolved in 42 c.c. of water and boiled on a sand-bath under a reflux condenser. During the course of two hours 50 grams of ethyl-*p*-toluene sulphonate were added; when the addition was complete the mixture was heated for a further half hour. The ethyl iodide was then distilled from a water-bath. The yield of dry, redistilled product was 26 grams or 66·6% of theory. When the ethyl toluene sulphonate was added all at once and the reaction completed by boiling for $2\frac{1}{2}$ hours, the yield was 25 grams. The gradual addition of the ethyl toluene sulphonate effects very little improvement in the yield.

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The Isomeric Transformation of *Allo*-cinnamylidene Acetic acid into the normal Form with Iodine as Photo-catalyst.

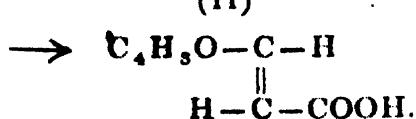
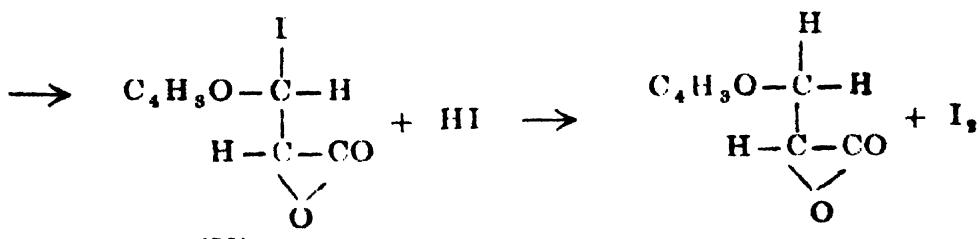
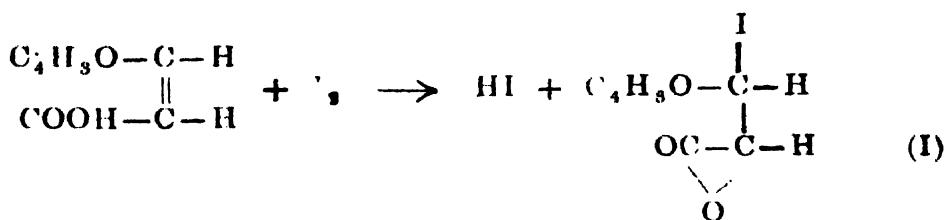
BY

JNANENDRA CHANDRA GHOSH

AND•

SAMARENDR A GUPTA.

Liebermann (*Ber.*, 1895, 28, 1446) discovered that *allo*-furfuraldehyde acrylic acid, *allo*-cinnamic acid and *allo*-cinnamylidene acetic acid are slowly transformed into the normal form under the influence of light but if iodine is simultaneously present the transformation is very rapid. He postulated the following mechanism for the transformation of *allo*-furfuraldehyde acrylic acid :



It will be noticed that the intermediate compounds I and II contain asymmetric carbon atoms, and it was

believed that the influence of polarised light on the velocity of this type of isomeric transformation, where asymmetric carbon atoms are present in the intermediate compound, might yield interesting results. The transformation of *allo*-cinnamylidene acetic acid into the normal form has been studied and it has been found that the velocity of transformation in chloroform solution is dependent on the intensity of light but not on its state of polarisation.

Allo-cinnamylidene acetic acid, $C_6H_5CH:CH\cdot CH:CH\cdot COOH$ was prepared according to Liebermann's method (*Ber.*, 1895, 28, 1441). He found that 0·6 grams of *allo*-acid and 0·1 gram of iodine dissolved in 12 c.c. of benzene exposed to mid-day sun gave crystals of normal acid in a minute, which, being difficultly soluble, separated out from benzene. Benzene, however, cannot be used as solvent in our experiments for two reasons :

(i) The separation of the end product as an insoluble solid would not be a case of photo-catalysis in homogeneous system.

(ii) The appearance of shining crystals of the normal acid, growing in size and depositing on the sides of the vessel, would very considerably change the intensity of the incident light by reflection and scattering and hence would make useless and unreliable all attempts to measure the amount of light absorbed by the reacting system.

The normal acid is sparingly soluble in most organic solvents; in chloroform, however, both the forms are fairly soluble and the velocity of isomeric transformation was measured in this solvent. Estimation of the quantity of the *allo*-form which has been changed in a definite interval of time to the normal form presented considerable difficulty. The normal acid has the melting point 165° , while the *allo*-acid has the melting point 136° .

and it was thought that the quantity of each variety present in the solid residue after evaporation of chloroform in the dark might be found out by determining the melting point of the solid residue. This method was, however, found to be unreliable as the melting point of the mixture was not at all sharp. The following method of estimation was, however, found to yield satisfactory results. 3 c. c. of the chloroform solution containing the *allo*-acid and iodine were taken out from the reaction cell and the time noted. It was poured into a long stoppered tube with a bulb at one end which contained perfectly anhydrous sodium thiosulphate. The iodine reacted on shaking with sodium thiosulphate and the solution became colourless. The chloroform was then evaporated in an air-oven whose temperature was never allowed to exceed 70°. Liebermann found that a benzene solution of the *allo*-form containing iodine, if boiled in a water-bath for half an hour, gives normal acid. The chloroform solution, when freed from iodine, did not, however, during the process of evaporation, produce any measurable quantity of normal acid as will be clear from the fact that very good monomolecular velocity coefficients could be obtained from the experimental data. Moreover, the velocity of this photochemical transformation is very much slower in chloroform than in benzene.

Pure and dry benzene was now poured over the solid residue in the bulb tube up to a mark in the stem, (vol. 4 c. c.) the stopper put on, and the tube shaken in a thermostat for an hour, and left undisturbed to obtain clear benzene solution. 2 c. c. of the benzene solution was sucked out by means of a pipette, fitted with glass-wool plug and the quantity of the total acid in the solution obtained by titration with fresh NaOH solution. The solubility of the normal acid in benzene at different temperatures was determined, from which

the quantity of the normal acid which passed into solution at the temp. of the thermostat could be determined. The solubility data in benzene are given in Table I.

TABLE I

Temp.	Gm. of normal acid in 1 c.c. of benzene $\times 10^3$
15°C	4.26
22°	5.29
30°	7.72
35°	10.0

The difference between the total acid and the normal acid gives the quantity of the *allo*-acid that has remained unchanged. It is essential for the success of the experiments that both sodium thiosulphate and benzene should be perfectly dry. Crystals of pure sodium thiosulphate were powdered and heated in an air-oven at 110° for several hours and kept in a vacuum dessicator over sulphuric acid. Iodine and choloroform were purified in the usual way.

A 1000 c.p. Pointolite lamp maintained by a constant current of 6.5 amperes was used as the source of light. The point arc, placed at the focal length of a powerful converging lens, gave a parallel beam of light which was passed successively through filters of $N\text{-KNO}_3$ solution (1 cm. thick) and $0.01N\text{-CuSO}_4$ solution (10 cms. thick). The reaction vessel was maintained at a constant temp. by enclosing it in a double jacketed metal box with a window, through whose annular space water from a thermostat was circulated by a pump. The temperature of this jacket could be maintained constant within $\pm 1^\circ$.

The experimental results are given below.

TABLE II

Concn. of iodine $2 \cdot 048 \times 10^{-2}$ gm. mol. per litre

Initial Concn. of *allo*-acid $1 \cdot 709 \times 10^{-1}$ " " "

Temp. $34 \cdot 3^{\circ}\text{C}.$

Time in mins.	Titre of NaOH sol. ($\cdot 0126\text{ N}$, equivalent to the conc. of <i>allo</i> -acid)	$k = \frac{1}{t} \log \frac{a}{a-x}$
0 *	12.9 c.c.	—
124	8.3 c.c.	.00154
219	6 c.c.	.00151
297	4.6 c.c.	.00150
393	3.1 c.c.	.00156
		Mean .00153

The reaction gives a good monomolecular constant as will be clear from Table II. In Table III are given the velocity coefficients for different concentrations of iodine.

TABLE III

Concn. of iodine	Concn. of <i>allo</i> -acid	k (mean)
$2 \cdot 048 \times 10^{-2}$	$1 \cdot 709 \times 10^{-1}$.00153
$1 \cdot 024 \times 10^{-2}$..	.00152
$.4096 \times 10^{-2}$..	.00158

* The first reading is taken after about 3 hours' exposure to light, when sufficient normal acid has been formed to give a saturated solution with benzene under the conditions of experiment, and this first reading in the table is given as corresponding to zero time.

It will be noticed from Table III that the velocity constants are independent of the concentration of iodine which is the photo-catalyst in the reaction. This is explicable only on the ground that the whole of the incident light within the photo-active region is absorbed by the lowest concentration of iodine used in our experiments. According to Plotnikow,

$$\frac{dx}{dt} = \frac{k}{p} \left[1 - e^{-\epsilon p(a-x)} \right] (b-x) \quad \dots \quad (1)$$

where $(a-x)$ is the concentration of the photo-active substance, $(b-x)$ that of the photo-inactive component.

Equation (1) reduces to

$$\frac{dx}{dt} = \frac{k}{p} (b-x) = k'(b-x) \quad \dots \quad (2)$$

if $e^{-\epsilon p(a-x)}$ is negligibly small or if variation in

$\left[1 - e^{-\epsilon p(a-x)} \right]$ is small.

$$\therefore k' = \frac{1}{t} \log \frac{b}{b-x}.$$

The extinction co-efficient of iodine in chloroform solution was measured by a Koenig Merten spectro-photometer and calculated from the equation

$$\frac{\log_{10} \tan \alpha^1 - \log_{10} \tan \alpha^2}{l_c} =$$

The values are given in the following table.

TABLE IV

Wave-length (λ)	Extinction co-efficient (ϵ)
6563	88×10^3
5876	$2 \cdot 1 \times 10^3$
5461	$5 \cdot 9 \times 10^3$
4861	$8 \cdot 9 \times 10^3$
4571	$4 \cdot 4 \times 10^3$

It will be seen that the extinction co-efficients have large values, and in our experiments with the lowest concentration of iodine the percentage of light absorbed are—

λ	Light absorbed	
6563	85.2%	apply.
5876	98.9%	"
5461	100%	"
4861	100%	"
4571	100%	"

Influence of Concentration of allo-acid on the Velocity Co-efficient.

The range of concentration available for experimental purpose is rather small due to the following reasons :—

- (1) The limited solubility of the *allo-acid* in CHCl_3 .
- (2) An appreciable solubility of the normal form in benzene in which the solid residue (a mixture of normal and *allo-acid*), on evaporation of chloroform, is dissolved for estimating the amount of *allo-acid* left over.

TABLE V

Initial concentration of *allo*-acid ... 3.418×10^{-1} gm. mols. per litre.
 Concentration of iodine ... 1.024×10^{-2} gm. mols. per litre.

Time in mins.	Titre of .0124 N— NaOH soln.	
0	32.2	...
85	25.5	.00119
160	22.5	.00097
263	17.5	.00100
315	15	.00102
		Mean .00105

The agreement between the individual values of velocity co-efficients are not so good as recorded before, but the mean value of the co-efficient is certainly less than .00150 in Table II. This is an anomaly, for in homogeneous unimolecular reactions the velocity constant is independent of the concentration of the substance undergoing transformation. The reason for this anomaly must be sought for in the fact that Equation (1) is not strictly accurate. If it were so, the rate of photochemical transformation would increase indefinitely as the concentration of the photo-inactive component increases, although the amount of light absorbed remains constant. This would mean a complete negation of Einstein's law of photochemical equivalence, which has been found to be true in some cases at least. The equation of Cario (*Zeit. Physik*, 1922, 10, 185), modified by Turner (*Phys. Review*, 1924, 23, 466),

$$\text{Rate} = c \left[\frac{1}{1 + \frac{1}{Aa^2 \tau p}} \right]$$

$$\text{Whence } \frac{1}{\text{Rate}} = \frac{1}{\text{Const.}} + \frac{1}{\text{Const.} \times p} \dots \dots \quad (4)$$

(where p is gas pressure of the photo-inactive component), which has been applied with success to photochemical

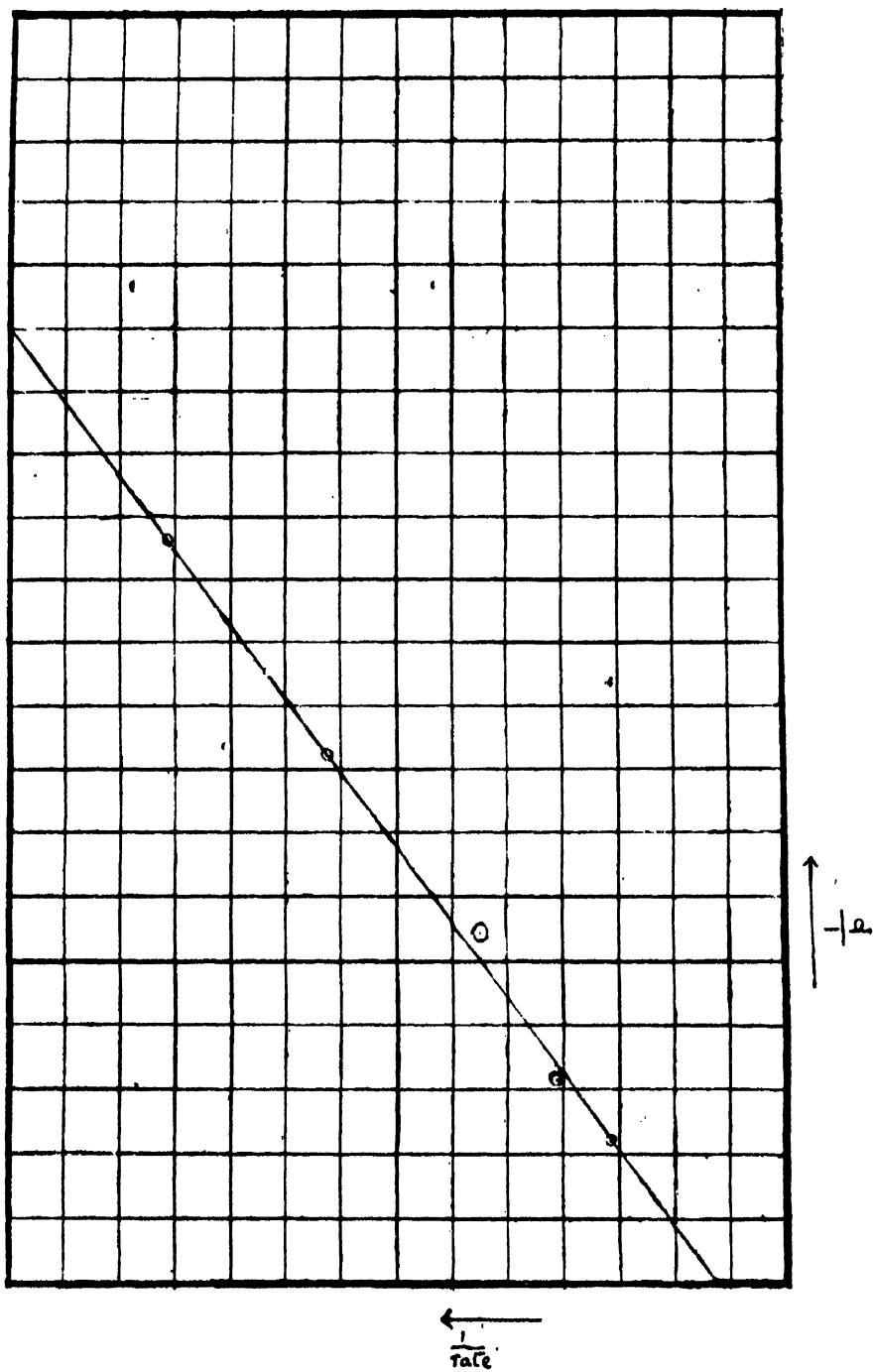


FIG. 1

Each side of a square = 5 units.

Each side of a square $\equiv 10^{-4}$ (mm.)

reaction in gaseous systems, gives a definite limiting value for the rate of transformation when the concentration of the acceptor molecules becomes infinite. According to Eq. (4) the increment in the value of $\frac{\Delta x}{\Delta t}$ with increment in pressure becomes less and less as the absolute value of the pressure becomes larger and larger. The extension of this equation to homogeneous photochemical reaction in solution has been tried by the substitution of the osmotic pressure for concentration. The graph of the inverse of rate of transformation against the inverse of osmotic pressure of acceptor molecules will be a straight line, the inverse of intercept representing the limiting rate of reaction for infinite concentration of the photo-inactive component. The values of $\frac{\Delta x}{\Delta t}$ cannot be very accurately determined for very small intervals of time because the method of estimation of the substance undergoing transformation is not at all sensitive in this case, but from Tables II and V we can obtain mean values of $\frac{\Delta x}{\Delta t}$ for mean values of concentration of *allo-acid*. This is given in the following Table.

TABLE VI

Rate	$\frac{1}{\text{Rate}}$	Mean concen. of <i>allo-acid</i>	$\frac{1}{p}$ (p in millimetre)
·0605	16·53	27·35	$22·9 \times 10^{-6}$
·0485	20·63	20	$31·1 \times 10^{-6}$
·0371	26·95	10·6	$55·7 \times 10^{-6}$
·0241	41·49	7·2	$82·9 \times 10^{-6}$
·0180	55·56	5·3	117×10^{-6}
·0150	64	3·85	162×10^{-6}

In Fig. 1 the inverse of the rate has been plotted against inverse of osmotic pressure and if we omit the last point, i.e., for the lowest concentration, all the points fall on a straight line; $1/\text{Rate}$ for infinite concen. of *allo-acid* is 7·5, or the rate of transformation is 133 for infinite

concn. of *allo*-acid. It is rather unfortunate that the velocity of the reaction for higher concentrations of *allo*-acid is not capable of direct experimental measurement. From Cario and Turner's equation we can, however, calculate the life period of the excited molecule. Since,

$$\text{Rate} = c \left[\frac{1}{1 + \frac{1}{A\alpha^2 \tau p}} \right]$$

where α is the mean distance between the centres of molecules, τ the life period and A , a constant equal in magnitude to

$$2666 \cdot 6 \sqrt{\frac{2\bar{N}}{k\theta} \cdot \frac{m_1 + m_2}{m_1 m_2}}$$

where m_1 and m_2 are the molecular weights of the photo-active and the acceptor molecules respectively, θ , the absolute temp. and k , the gas constant per molecule, it is evident that when $\frac{1}{\text{rate}}$ is plotted against $\frac{1}{p}$,

$$A\alpha^2 \tau = \frac{\text{Intercept}}{\text{Slope}} \text{ of the graph.}$$

The intercept is 7.5 and the slope = (4.5×10^4) and $A = 2.52 \times 10^{21}$.

Putting $\alpha = 3 \times 10^{-8}$, $\tau = 8 \times 10^{-10}$ sec. This is slightly less than the life period of activated molecules by other methods and the average value is about 10^{-8} .

Application of Einstein's Law of Photo-Chemical Equivalence.

Radiant energy from a Hefner lamp at a distance of 1 metre produced a galvanometer deflection of 25 divisions. The light absorbed by the lowest concn. of iodine is equivalent to 689 divisions of galvanometer. The thickness of the reaction vessel used was 1 cm. Energy absorbed per sq. cm. per second

$$= \frac{689 \times 900}{25} \text{ ergs.}$$

Assuming the mean wave-length of efficient light to be $500\mu\mu$, $h\nu$ becomes $3 \cdot 9 \times 10^{-12}$ ergs.

Therefore the number of quanta in the absorbed energy = $6 \cdot 35 \times 10^{15}$

The change in the *allo*-acid in 393 minutes (see Table II) in 1.5 c.c. of the solution corresponding to a surface of 1.5 sq. cm. = 9.8 c.c. of 0.0126*N* alkali.

Therefore, the number of molecules transformed per sec. per sq. cm.

$$\frac{9.8 \times 0.0126 \times 6.3 \times 10^{15}}{60 \times 393 \times 1000 \times 1.5}$$

Therefore,

$$\frac{\text{The no. of quanta}}{\text{The no. of molecules}} = 2.8$$

that is, 2.8 quanta are necessary for the transformation of 1 molecule of *allo*-acid. For higher concentration of *allo*-acid change in 1.5 c.c. in 160 minutes = 9.7 c.c. of 0.0124*N* alkali (see Table V). Here 1.2 quanta transform 1 molecule of *allo*-acid. For infinite concentration of *allo*-acid, assuming that the extrapolation value is justified in Curve 1 :—

Change in *allo*-acid per minute = 133 c.c. of 0.0124*N* alkali. Hence one quantum transforms in the limiting case 1.8 molecules of *allo*-acid.

Temperature Co-efficient of the Reaction.

The velocity co-efficient of the reaction at $24 \cdot 3^\circ$ was found to be 0.00087, concentration of *allo*-acid being $1 \cdot 709 \times 10^{-1}$ gm. mol. per litre and that of iodine $1 \cdot 024 \times 10^{-2}$ gm. mols. per litre.

The temperature co-efficient is, therefore, $\frac{0.0152}{0.00087} = 1.75$

Influence of the State of Polarisation of Light on the Velocity Co-efficient.

The intensities of the parallel beams of ordinary light and plane polarised light were made approximately equal by suitable choice of lenses. The light filters used were always identical and in the case of ordinary light, a film of Canada balsam between two plane parallel glass plates, were interposed between the reaction cell and the source of light to compensate any effect that the film of Canada balsam in the Nicol might produce in the case of polarised light.

Intensity of incident plane polarised light

= 234 divisions of galvanometer (a resistance of 33 ohms was in the circuit of the galvanometer).

Change in *allo*-acid in 10 hours = 10.7 c.c.

Intensity of incident ordinary light under the same conditions = 239 divisions.

Change in *allo*-acid in 10 hours = 11 c.c.

In another set of experiments the intensities of plane polarised and circularly polarised light were similarly made almost equal. It was found that the velocity of transformation is independent of the quality of polarisation of absorbed light.

Intensity of plane polarised light (with 30 ohms resistance in the circuit of the galvanometer) = 405 divisions.

Change in *allo*-acid in 10 hours = 17.05 c.c.

Intensity of circularly polarised light under the same conditions = 387 divisions.

Change in *allo*-acid in 10 hours = 16.9 c.c.

Hence, there is practically no change in the velocity co-efficients due to the change in the state of polarisation of the incident light.

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A Critical Study of the Methods of Analysis of Lignin.

BY

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The problem of estimating lignin in lignocelluloses has attracted much attention in recent years. The pioneers in the field are Cross, Bevan and Briggs (*Ber.*, 1907, 40, 3119) who regarded the maximum absorption of phloroglucinol under standard conditions as a new chemical "constant" of the lignocelluloses. All the direct methods for estimating lignin may be classified as acid hydrolysis and alkali extraction processes.

Among the former may be mentioned those of Ost and Wilkening (*Chem. Zeit.*, 1910, 34, 461), Willstätter and Zechmeister (*Ber.*, 1913, 46, 2401) and Wenzl (*Papierfabr.*, 1922, 22, 101). Various workers such as Beckmann (*Z. angew. Chem.*, 1921, 34, 285), Paschke (*Cellulosechemie*, 1922, III, 19), Powell and Whittaker (*J. Chem. Soc.*, 1924, 125, 357) have isolated lignin by extracting the substance with sodium carbonate or hydroxide solutions and precipitating the lignin by the addition of acid. Alkali extraction methods are as a class more tedious and give lower yields than acid hydrolysis methods and are therefore not suitable for quantitative analytical purposes. The recent method proposed by Schimidt (*Ber.*, 1923, 56B, 23) by treating the substance with an aqueous solution of chlorine dioxide is very unsatisfactory and is open to several objections which have been discussed in detail by Heuser (*Ber.*, 1923, 56B, 902). In the present paper a critical study is made of the determination of lignin by acid hydrolysis methods and its reaction with phloroglucinol.

EXPERIMENTAL.

Finely powdered rice straw after extraction with ether for 3 to 4 hours was taken for all the experiments described below. The following results show that extraction of the straw with ether to remove the fat and resin is necessary before hydrolysing it with the acid. Higher results were uniformly obtained with the unextracted samples, the increase just accounting for the ether extract and a slight amount of residue was left after removing the lignin by chlorination which could not be further hydrolysed with sulphuric acid and which completely dissolved in ether.

TABLE I

Substance	% yield of lignin	% of the residue after the second chlorination	% solubility of the lignin in ether
Rice straw extracted with ether.	23.97	0.08	Nil
Do. before extraction with ether.	25.82	1.7 (soluble in ether)	1.5

Chlorination of Lignin.—In order to find out whether any cellulose was left unattacked after the acid hydrolysis, the lignin obtained by the different methods was chlorinated. After draining off the water under the pump the asbestos pad, containing the lignin, was chlorinated in a small beaker by passing a slow stream of washed chlorine for 15 minutes and stirring frequently with a pointed glass rod. Rapid reaction ensued and the substance became brown in colour. The chlorolignin was removed by digesting with 2 per cent. sodium sulphite solution and the residue after washing was chlorinated as above for another ten minutes for the complete removal of lignin. The percentage of residue left after the second chlorination of the lignins obtained by the different methods is given in Table III.

Phloroglucinol Absorption of Lignin.—This was determined by the method described in detail by Cross, Bevan and Briggs (*Chem. Zeit.*, 1907, 31, 725). The dried substance was treated at the room temperature for 18 hours with standard phloroglucinol solution and the excess of the phenol titrated with formaldehyde using as indicator the colour reaction of the phenol with lignocellulose, ordinary "news" printing paper being taken as test paper. The phloroglucinol filtrate of the straw was much more intensely coloured than in the case of lignin or the straw which was boiled with 12 per cent. hydrochloric acid. The filtrates of the latter were practically colourless. Pure cellulose does not show any absorption of the phenol. The phloroglucinol absorption values, which were determined, are tabulated below.

TABLE II

Substance	% of phloroglucinol absorbed calculated for 100 gms. of the dry straw	% of CHO in 100 gms. of lignin calculated from the phloroglucinol absorption value
1. Straw.	10·55	10·12
2. Straw which was boiled with 12 % HCl for $\frac{1}{2}$ hour under reflux, washed and dried.	4·20	4·03
3. Straw freed from furfural-yielding bodies by repeated distillation with 12% HCl, washed and dried. (Krober's method.)	4·13	3·96
4. Lignin obtained by the sulphuric acid method.	4·05	3·89
5. Lignin obtained by the hydrochloric acid method (without boiling the acid).	4·32	4·30
6. Lignin obtained by the HCl method (after boiling the acid).	4·10	4·09
7. Lignin obtained by Wenzl's method ...	3·80	4·06
8. Residue after the second chlorination of lignin (first chlorination 15 minutes; 2nd chlorination 10 minutes).	Nil	Nil

Sulphuric Acid Method.--72% sulphuric acid is a very convenient reagent for hydrolysing cellulose. Complete hydrolysis is effected by digesting the substance with the acid for about 16 hours. There is considerable difficulty in filtering the lignin residues owing to the colloidal nature of the solution, even when a more dilute acid is used as recommended by Klason (*Cellulosechemie*, 1923, 4, 81). This can be overcome by diluting and boiling the solution. The following results show the effect of boiling on the yield of lignin :—

Time of boiling	% yield of lignin
Not boiled	26.46
15 minutes	24.21
20 minutes	24.01
60 minutes	23.97
120 minutes	23.98

It will be noted that the action is complete after half an hour and that no further loss takes place on continued boiling. In view of the above results the following procedure was adopted for the determination of lignin by this method. One gram of the air-dried material after extraction with ether was treated with 15 c.c. of 72% sulphuric acid in a well stoppered bottle and the mass intimately stirred with a glass rod. After hydrolysis at room temperature for 20 hours the acid was diluted to a concentration of 3% and the solution boiled under a reflux condenser for one hour. The lignin was then filtered through asbestos, thoroughly washed, dried at 105°,

weighed and ignited, and the percentage of ash-free lignin was calculated from the difference. The substance thus isolated is an amorphous dark powder insoluble in water and readily soluble in alkalis and ammonia.

Hydrochloric Acid Method.—Whereas ordinary concentrated hydrochloric acid (37% HCl) decomposes and gelatinises cellulose after about a day's action, a more concentrated acid (41-42% HCl) dissolves cellulose completely within a short time. The undissolved residue is lignin. The filtrate is slightly dark coloured, and a black precipitate is formed on diluting with water and boiling. When this precipitate is chlorinated for 7 or 8 minutes it becomes grey coloured and completely dissolves in a 2 per cent. solution of sodium sulphite giving the brilliant magenta colour produced by chlorolignin. The precipitate is therefore lignin which had passed with the filtrate in a colloidal state. The determination of lignin by this method was therefore done as follows:—One gram of the substance was treated with 20 c.c. of 42% hydrochloric acid for 24 hours at the room temperature. The solution was then diluted to a concentration of 12 per cent., boiled for 30 minutes under a reflux condenser, filtered through asbestos and the lignin estimated as usual. By prolonging the time of exposure of the straw to the acid for two or three days, higher yields were obtained probably due to the formation of lignin hydrochloride.

Wenzl's Method.—The reagent was prepared by gradually adding 25 gms. of phosphorus pentoxide to 100 gms. of fuming hydrochloric acid ($d\ 1.19$) while cooling with ice. The filtrate obtained on digesting the substance with this reagent contained some lignin in a colloidal form. One gram of the substance was therefore digested with 20 c.c. of this reagent for 24 hours, the solution diluted to 80 c.c. with water, boiled for 30 minutes and the lignin estimated. The following table gives the yields

and nature of the lignins obtained by the different methods:—

TABLE III

Method	% of lignin in the dry straw	Residue left after the removal of lignin by chlo- rination	% of furfural- dehyde in the hydrochloric acid distillate of the lignin
Sulphuric acid method	23.97	0.08	Trace
Hydrochloric acid method	23.10	0.15	Do
Wenzl's method	21.54	0.24	Do

Discussion of Results and Conclusion.

Cross and Bevan state that the phloroglucinol absorption value is characteristic of lignocelluloses "proportional to the degree of lignification of the substance and independent of the furfural-yielding constituents." It is, however, found that the absorption of the phloroglucinol by the straw is about $2\frac{1}{2}$ times as great as that of the lignin isolated from it. This large difference may be due to (a) decomposition of the lignin present in the straw during the process of isolation, or (b) absorption of the phenol by other groups present in the lignocellulose in addition to that of lignin or both. As lignin is highly resistant to acids it is not likely that any decomposition could have occurred in isolating it by acid hydrolysis methods. Any such loss is a negligible factor. This is seen from the fact that straw, which was washed and dried after boiling with dilute hydrochloric acid just for 30 minutes, shows almost the same absorption of phloroglucinol as the lignin isolated by digesting the substance for 24 hours with 42% HCl and diluting and boiling the solution for half an hour. If

there be any decomposition of the lignin a considerable difference between the two values might be expected. The second cause is therefore more important and it is shown that the increase in the absorption of phloroglucinol is almost entirely due to the presence of furfural-yielding bodies in the lignocellulose. Thus straw, from which furfural-yielding constituents are removed by distillation with dilute hydrochloric acid, shows practically the same absorption of the phenol as the lignin (see Table II).

The product of the reaction between lignin and phloroglucinol is the formation of lignin phloroglucide due to the presence of the aldehyde group in the lignin molecule. Beckmann and Ziesche (*loc. cit.*; also *Biochem. Z.*, 1921, 121, 293) give the formula $C_{39}H_{43}O_{14}CHO$ for lignin isolated from straw while according to Paschke, (*loc. cit.*) it has the formula $C_{39}H_{44}O_{14}CHO$. The percentage of CHO group in lignin calculated from the above formula is 3.78. The results given in Table II show that the figure for lignin calculated from the phloroglucinol value is 3.9 which closely agrees with the theoretical value. Lignin prepared from a different sample of straw gave the same phloroglucinol value as above, though the absorption of the phenol by the two samples of straw in their "natural" state showed considerable difference.

The reaction between phloroglucinol and lignocellulose is therefore in two directions, *viz.*, (1) the combination of the lignin group with the phenol and (2) the absorption of the phenol by the furfural-yielding groups in the substance, the first reaction producing a colourless compound and the second forming a coloured derivative.

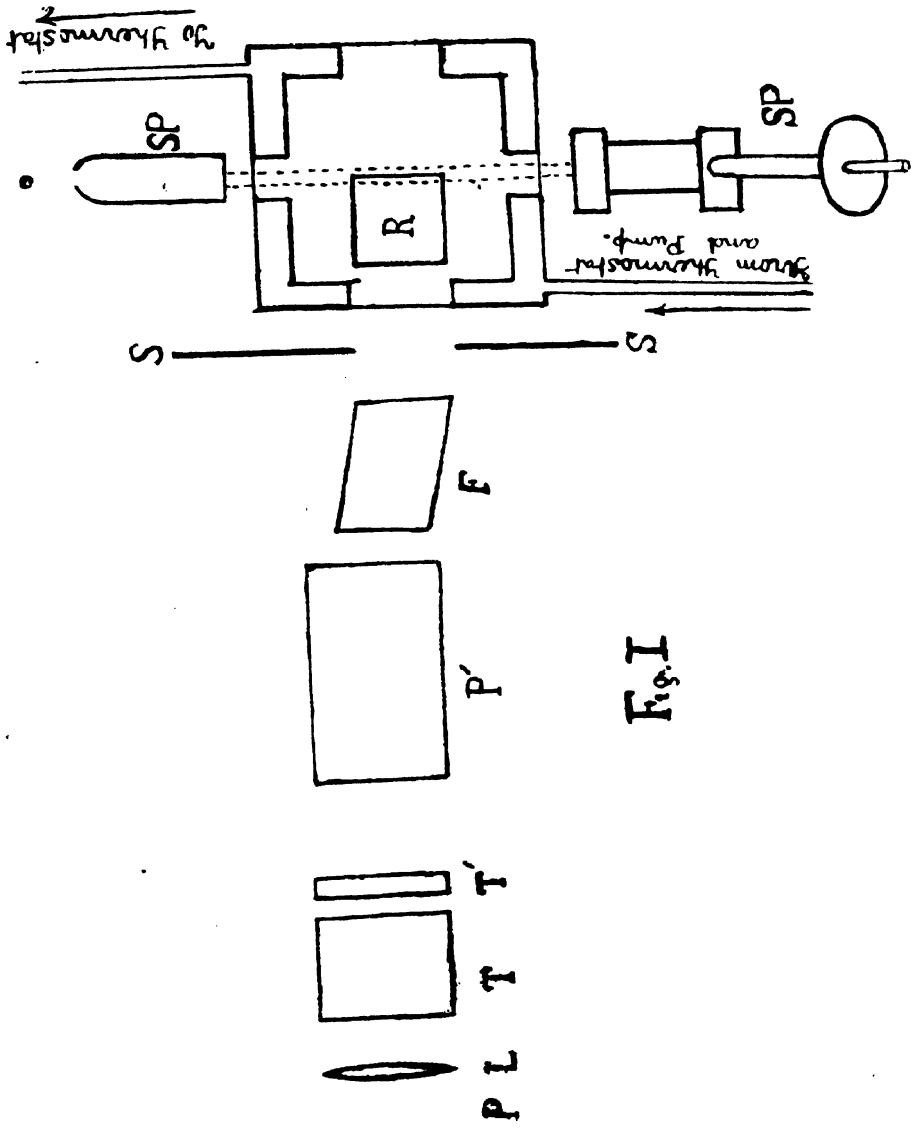
The sulphuric acid method gives the maximum yield of lignin. No residue is left after the second chlorination and the substance is practically free from pentosans.

This method is the most convenient and is free from the drawbacks which accompany the other processes. In the hydrochloric acid method it is necessary to dilute and boil the solution after digesting the lignocellulose with acid in order to avoid the loss of lignin in a colloidal state. A slightly lower yield is obtained but the method may be considered satisfactory. Wenzl's method is not suitable for the quantitative determination of lignin as the reagent attacks the lignin molecule. The yield of lignin and the phloroglucinol value are much lower than the corresponding figures obtained by the other two methods. For isolating and estimating lignin the sulphuric acid method is therefore recommended.

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Photochemical Reactions in Circularly Polarised, Plane Polarised and Ordinary Light.

The Velocity of Reactions between Bromine and
(1) Cinnamic Acid, (2) Stilbene.

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The reaction between bromine and cinnamic acid has been investigated by Herz and Mylius (*Ber.*, 1906, 39, 3816), and that between bromine and stilbene by Bauer and Moser (*Ber.*, 1907, 40, 918). The dibromo derivatives are stable in both cases, and the reactions proceed to completion. The velocity of these reactions in darkness is negligibly small when carbon tetrachloride is used as solvent.

Byk (*Z. physical. Chem.*, 1904, 49, 641) suggested that synthesis of a compound containing asymmetric carbon atom by circularly polarised light might lead to the formation of one of the optical isomers in a preponderating ratio; but the recent work of Bredig (*Z. angew. Chem.*, 1923, 62, 456) has not confirmed this hypothesis. From the present investigation it appears very probable to us that the velocity of the above reactions does not only depend on the intensity of light but also on the quality of light.

EXPERIMENTAL

A Point-o-lite 100 c.p. lamp *P* (Fig. 1) was run at 110 volts from a battery of accumulators; *L* was a convex lens

for obtaining a parallel beam of light. T and T' are rectangular glass vessels with plane parallel sides filled with $N/50$ copper sulphate solution (4 cm. thick) and with normal potassium nitrite solution (1 cm. thick) respectively. The first filter cuts off heat rays completely and part of the red light and the second, ultraviolet radiations beyond $390 \mu\mu$ (*vide* Ghosh and Biswas, *Z. Elektro-chem.*, 1924, 30, 97). The polariser P' consisted of a large nicol, 4.5 cm. aperture, which gave a horizontal beam of polarised light. It was so arranged that the plane of polarisation of the emergent beam was inclined at an angle of 45° to the horizontal plane. The Fresnel Rhomb F was set up with its faces vertical, and the emergent circularly polarised light passed through the aperture (2.5 cm. \times 2.5 cm.) of a screen S , into the reaction vessel R (2.5 \times 2.5 \times 2 cm.). This vessel was enclosed in a double jacketed copper box with plane parallel glass windows through which water was continuously circulated from a thermostat by means of a pump. The temperature was kept constant within $\pm 0.1^\circ$. The intensity of light was measured by means of a radio-micrometer placed behind the copper box and was varied by using lenses of different focal lengths, the point arc of the lamp being always at the focal distance of the lens. When ordinary parallel light was used for experiment, a canada balsam film between two plane glass plates was interposed between the screen S and the filters, so that light, in all the experiments recorded here, passed through a film of canada balsam. It is well known that the absorption and reflection co-efficient of colourless optical glass is independent of wave-lengths between $760 \mu\mu$ and $390 \mu\mu$ and therefore the distribution of intensities of light over the various wave-lengths remained identical in experiments with ordinary, plane polarised and circularly polarised light. As a matter of fact the

transmission co-efficient of plane parallel glass plates used in these investigations was about 98%.

The concentration of bromine in the reaction chamber was measured by means of König Martens Spectrophotometer, *SP*. Table I gives the concentration of bromine corresponding to $\log \frac{\tan \alpha}{\tan \alpha_0}$ for the green light ($546\mu\mu$) used in these measurements. The exact proportionality between the concentration and $\log \frac{\tan \alpha}{\tan \alpha_0}$ is evident and hence concentration of bromine can be easily calculated by interpolation from this table.

TABLE I

Concentration of bromine	$\log \frac{\tan \alpha}{\tan \alpha_0}$
.01742	.6925
.01635	.6464
.01348	.5333
.01214	.4718
.01012	.3933
.00967	.3418
.00639	.2578
.00485	.1948
.00323	.1275

Bromine, stilbene, cinnamic acid and carbon tetrachloride (used as solvent) were all obtained from Kahlbaum and were further purified in the laboratory.

The molecular extinction co-efficient of bromine for light transmitted through the filters used in this investigation as measured by the radio-micrometer is given in Table II.

TABLE II

Light through cell	Deflection of radio-micrometer	Molecular extinction co-efficient of bromine for light transmitted through filters
(1) Filled with CCl_4 . . .	261	...
(2) Filled with .01623 Mol. Br solution.	223	1.68
(3) Filled with .00811 Mol. Br solution.	239	1.88

TABLE III

Cinnamic acid0425 M
Bromine01825 M
Temp.	26°C

Intensity of light = 228 mm. deflection of radiomicrometer.

Time in minutes	Conc. of Br	$k \times 10^5$
0	.01825	...
35	.01357	823
65.5	.01057	833
97	.00817	826
130	.00653	820
167	.00465	817

In Table III the velocity co-efficients are calculated on the basis of a unimolecular equation and it is evident that the values are identical within the limits of experimental error.

From Table IV it will be further noticed that the velocity constant is not exactly proportional to the intensity of incident light. The reason for this anomaly is not clear.

TABLE IV(a)

Temp.	Cone. of Br	Cone. of cinnamic acid	Intensity with aqueous filter only	$k \times 10^5$
26°	.0182 M	.0429 M	160	423
26°	.0182 M	.0429 M	360	817

TABLE IV(b)

Temp.	Cone. of Br	Cone. of stilbene	Intensity with aqueous filter only	$k \times 10^5$
26°	.0182 M	.022 M	160	283
26°	.0182 M	.022 M	360	570

Table V makes it quite clear that the velocity co-efficient is quite independent of the initial concentration of bromine but increases as the initial concentration of stilbene increases. The intensity of light was throughout the same in all these experiments.

TABLE V

Temperature—. 6°C.

Cone. of Br	Cone. of stilbene	$k \times 10^5$
.0182 M	.022 M	476
.0091 M	.022 M	483
.0118 M	.022 M	478
.0118 M	.011 M	446

Exactly similar results have been found in the bromination of cinnamic acid. According to present theories of photochemical reactions the photo-active molecules get excited by the absorption of radiant energy, and the

end products are the results of dark reaction which might be the spontaneous decomposition of these excited molecules. If this view were correct then in the reaction between bromine and stilbene or cinnamic acid, the latter must be considered as the acceptor molecules, while bromine should be regarded as the photo-active molecule which gets excited by the absorption of radiant energy. The rate of production of excited bromine molecules per unit volume of solution is proportional to the amount of radiation absorbed at any instant and is given by

$$\frac{d[\text{Br excited}]}{dt} = K I_0 \left[1 - e^{-\epsilon(a-x)} \right]$$

where $(a-x)$ is the concentration of bromine at any instant and I_0 is the intensity of incident light and ϵ , the molecular extinction co-efficient.

Now we have already seen that the value of ϵ is small (*vide Table II*) and therefore

$$\left[1 - e^{-\epsilon(a-x)} \right]$$

may be taken to be equal to $\epsilon(a-x)$.

The rate of production of excited bromine molecules is thus proportional to the concentration of bromine molecules at any instant for the same intensity of incident radiation and is given by $K I_0 \epsilon (a-x)$. Now if τ be the life period of excited molecules and T be the interval between two successive collisions between an excited bromine molecule and an acceptor stilbene molecule then the rate of production of stilbene dibromide is given by

$$K I_0 \epsilon (a-x) \frac{\tau}{T+\tau} \quad (\text{Turner, } \textit{Phys. Rev.}, 1924, 23, 464)$$

The rate of production of stilbene dibromide is the same as the rate of disappearance of bromine and therefore

we obtain

$$\frac{dc}{dt} = KI_0 \epsilon(a-x) \times \frac{\tau}{T+\tau}$$

which is the equation for a monomolecular reaction provided T remains constant during the progress of the reaction. The constant k , for monomolecular reaction is therefore equal to

$$KI_0 \epsilon \frac{\tau}{T+\tau} \quad \text{or} \quad C \frac{\tau}{T+\tau} \quad \text{where } C = KI_0 \epsilon.$$

Now assuming that the kinetic theory can be extended to dilute solutions,

$$T = \frac{1}{Aa^2 p}$$

where $A = 2666 \cdot 6 \sqrt{\frac{2\pi N}{K}} \cdot \frac{m_1 + m_2}{m_1 m_2}$

(m_1 and m_2 are the molecular weights of bromine and stilbene respectively; N, Avogadro number, and $K=1 \cdot 37 \times 10^{-16}$; a , the distance between the centres of two reacting molecules and p the osmotic pressure of the acceptor molecules in millimeters of mercury. It is clear that T remains constant during the progress of a reaction if p remains constant, i.e., if the concentration of the acceptor molecules is in excess. This has been always the case in our experiments.

It will be noticed that the value of K_1 should be independent of the concentration of bromine which has been actually found to be the case. The value of K_1 should, however, depend on the value of T, i.e., on p , the osmotic pressure of acceptor molecules.

$$K_1 = C \frac{\tau}{T+\tau} = C \frac{1}{1 + \frac{T}{\tau}} = C \frac{1}{1 + \frac{1}{Aa^2 p \tau}}$$

$$\text{or } \frac{1}{K_1} = \frac{1}{C} \left[1 + \frac{1}{Aa^2 p \tau} \right] = \frac{1}{C} + \frac{1}{CAa^2 p \tau}$$

that is, the inverse of the velocity constant should be a linear function of the inverse of the osmotic pressure of acceptor molecules and hence of the concentration.

The values of the velocity constants for varying initial concentration of cinnamic acid and the same initial concentration of bromine, the intensity of radiation remaining same in all the experiments, are given in Table VI. It will be seen that as the initial concentration of cinnamic acid increases the velocity co-efficient also increases and in Fig. II, graph I is plotted by taking $1/k_1$ as abscissa and $1/p$ as ordinate. It will be evident that as required by theory, the graph obtained is a straight line. From the slope of the curve and the value of the intercept on the abscissa, we can, following Turner, calculate the life period of excited bromine molecules.

$$\text{Slope} = \frac{1}{CAa^2\tau} \text{ and Intercept} = \frac{1}{C}$$

$$\text{Therefore } \frac{\text{slope}}{\text{intercept}} = \frac{1}{Aa^2\tau}$$

TABLE VI

Temp.	Cone. of Br	Osmotic pressure of cinnamic acid in mm. calculated from concentration	K_1 (velocity co-efficient)
24.5°	.005485 M	160.8	.03015
		120.6	.02668
		80.4	.02406
		60.3	.02077
		40.2	.01674
		30.15	.01440
		20.1	.01122

In this case the value of A is 27.29×10^{20} and from the curve the value of $Aa^2\tau$ is found to be 21.5×10^{-8} assuming $a=10^{-7}$ cm. the value of τ comes out to be 0.8×10^{-6} sec.

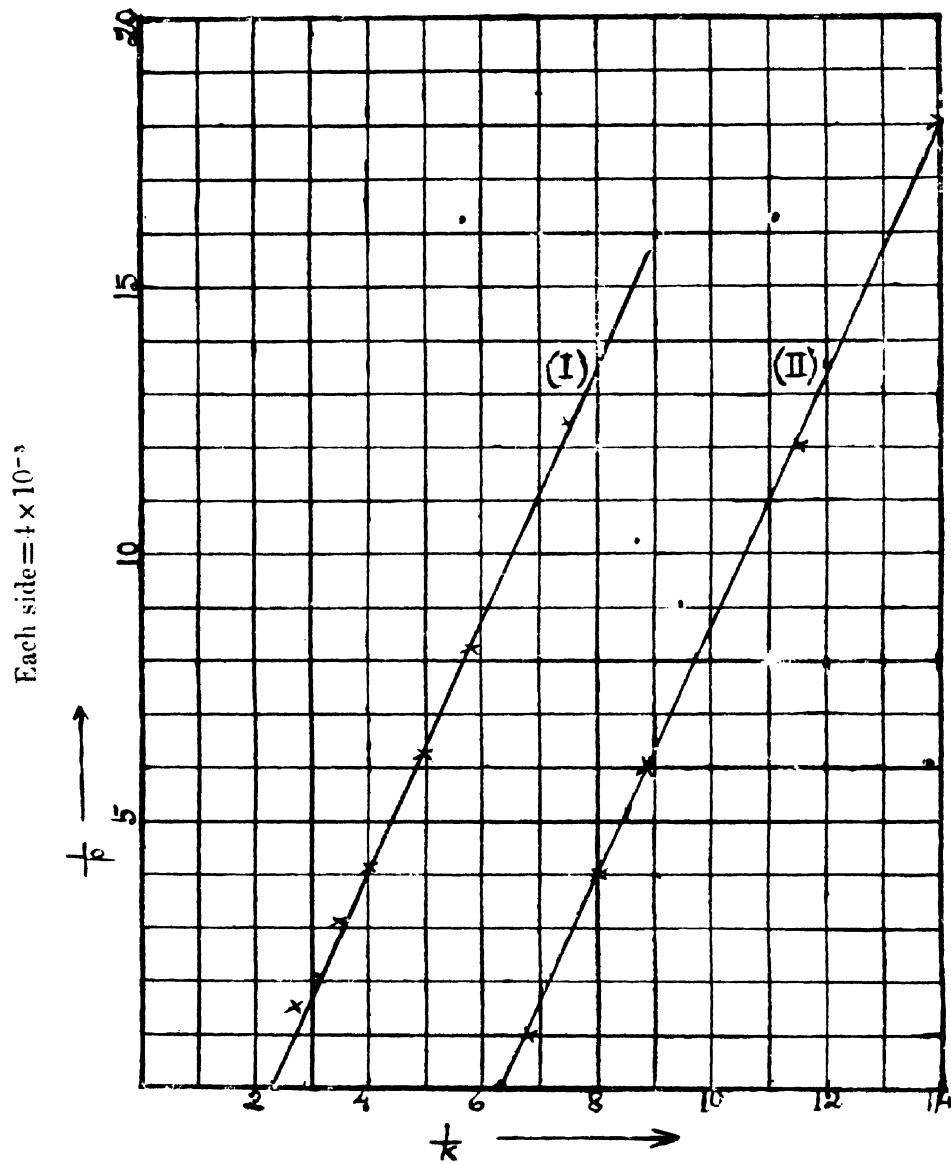


FIG. II.
Each side = 12 units

TABLE VII

Temp.	Cone. of Br	Osmotic pressure of stilbene in mm. calculated from concentration	K_1 (velocity co-efficient)
24°	.005485 M	249.7	.012
		62.43	.01035
		41.62	.00943
		20.81	.00722
		13.87	.00596

Table VII gives the values of velocity co-efficients for varying initial concentration of stilbene, and in Fig. II, graph II is plotted by taking $1/k$ as abscissa and $1/p$ as ordinate. Here too the requirements of theory are fulfilled for the graph is a straight line.

From the curve, $\Lambda a^2 \tau = 60.5 \times 10^{-3}$ and in this case A is 26.01×10^{20} . This gives $\tau = 2.33 \times 10^{-9}$ sec.

*Velocities of Photo-bromination for the same Intensities
of Ordinary, Plane Polarised and Circularly
Polarised Light.*

The intensities of plane polarised, circularly polarised and ordinary light were made as far as possible the same by suitable selection of lenses and placing the point arc at the focal distances of the lenses. The current and the voltage used for the lamp were never varied. Hence the distribution of intensities over the various frequencies in the beam of white light remained the same in all experiments. As has been already mentioned before, the absorption and reflection co-efficients of the glasses are the same for all wave-lengths between 760 and 400 $\mu\mu$ and therefore the quality of light in these experiments is identical excepting for the state of polarisation.

Tables VIII—XIII give the velocity co-efficients for photo-bromination of cinnamic acid and of stilbene in ordinary plane polarised and circularly polarised light. The experimental data for each experiment are reproduced in detail so as to indicate the relative variation in the values of the velocity co-efficients. Again each experiment was repeated several times and the reproducibility of the velocity co-efficients is shown by recording the data obtained in a duplicate experiment. In Tables XIV and XV is given a summary of the results. It will be noticed that for the same intensity, ordinary light and plane polarised light are equally effective, while circularly polarised light appears to be less effective. We do not intend at present to lay great stress on this observation, but unless there has been a systematic error in our observations or in our experimental arrangement, which we have not been able to detect, the data recorded here appear convincing.

TABLE VIII

Concentration of cinnamic acid— 0425 M Concentration of bromine — 01825 M Temperature — 26°C *Ordinary Light.*

Intensity of radiation = 229 mm. of radio-micrometer deflection.

Time	Conc. of Br	$K_1 \times 10^6$	Time	Conc. of Br	$K_1 \times 10^6$
0	·01825	—	0	·01825	—
40	·0132	810	30	·0143	812
80	·0098	832	65	·01053	843
180	·0064	805	94	·00821	814
185	·00401	826	145	·0057	803
240	·0038	(738)			
		Mean 818			Mean 818

$$K_1 = 818 \times 10^{-6}$$

TABLE IX

Plane polarised Light.

Intensity of radiation = 228 mm. of radio-micrometer deflection.

Time	Cone. of Br	$K_1 \times 10^5$	Time	Cone. of Br	$K_1 \times 10^5$
0	.01825	—	0	.01825	—
35.5	.01357	835	36	.0135	835
65.5	.01057	832	76.5	.009525	839
97	.00817	828	108	.007425	830
127	.00653	807	142	.0057	816
167	.00465	816	188	.00401	805
		Mean 824			Mean 825

$$\text{Hence } K_p = 825 \times 10^{-5}$$

TABLE X

Circularly polarised Light.

Intensity of radiation = 218 mm. of radio-micrometer deflection.

Time	Cone. of Br	$K_1 \times 10^5$	Time	Cone. of Br	$K_1 \times 10^5$
0	.01825	—	0	.01825	—
35	.01395	766	38	.01365	741
69	.01068	775	72	.01057	757
100	.00843	770	117	.00761	748
150	.006	741	154	.00577	745
209	.0041	(713)			
		Mean 764			Mean 748

$$\text{Hence } K_c = 756 \times 10^{-5}$$

Concentration of stilbene---.022 M

Concentration of bromine---.01825 M

Temperature ---26°C.

TABLE XI

Ordinary Light.

Intensity of radiation = 229 mm. radio-micrometer deflection.

Time	Conc. of Br	$K_1 \times 10^4$
0	.01825	—
40	.0147	540
75	.01241	513
120	.0099	508
160	.0084	(483)
		Mean 520

$$\text{Hence } K_s = 520 \times 10^{-5}$$

TABLE XII

Plane polarised Light

Intensity of radiation = 228 mm. radio-micrometer deflection.

Time	Conc. of Br	$K_1 \times 10^4$	Time	Conc. of Br	$K_1 \times 10^4$
0	.01825	—	0	.01825	—
49	.01395	547	70	.01252	538
99	.0108	529	109	.01038	526
150	.0087	497	165	.00847	495
		Mean 524			Mean 519

$$K_p = 522 \times 10^{-5}$$

TABLE XIII

Circularly polarised Light.

Intensity of radiation = 218 mm. radio-micrometer deflection.

Time	Conc. of Br	$K_1 \times 10^4$	Time	Conc. of Br	$K_1 \times 10^4$
0	.01825	—	0	.01825	—
59	.01372	485	53	.01402	496
101	.01132	472	100	.011325	476
162	.009	437	160	.008942	446
230	.00705	433	204	.00772	433
		Mean 457			Mean 463

$$K_c = 460 \times 10^{-6}$$

TABLE XIV

Temp.	Conc. of Bromine	Conc. of Cinnamic acid.	I.	$K_e \times 10^{-5}$	I,	$K_e \times 10^{-5}$	Ic	$K_c \times 10^{-6}$
26°C	.01825 M	.0425 M	229	818	228	826	218	756

TABLE XV

Temp.	Conc. of Bromine	Conc. of Stilbene	I.	$K_e \times 10^{-5}$	I,	$K_e \times 10^{-5}$	I.	$K_e \times 10^{-5}$
26°C	.01825	.022 M	229	520	228	522	218	460

Temperature Co-efficient of K.

The majority of photochemical reactions have very small temperature co-efficients; for a large number of reactions the value is unity (Plotnikow, *Lehrbuch der Photochemie*, p. 63). Dhar (*J. Chem. Soc.*, 1923, 123, 1857) gives for the reaction between potassium oxalate and iodine, sodium formate and mercuric chloride, the high

values 2.68 and 2.94 respectively. As Tables XVI and XVII will show the temperature co-efficient of these reactions is 2.6—2.8.

TABLE XVI

Temp.	Cone. of Br	Cone. of Stilbene	$k_1 \times 10^3$
23°	.01175	.022	214
83°	"	"	561
43°	"	"	1424

TABLE XVII

Temp.	Cone. of Br	Cone. of cinnamic acid	$k_1 \times 10^3$
32.5°	.01618	.0429	807
42.5°	.01618	..	2272

Tolman (*J. Am. Chem. Soc.*, 1923, 45, 2285) considers that molecules in the lower quantum states may not be in a condition to absorb radiant energy of the frequency used or the energy level, which they attain after the absorption, may not be high enough to lead to chemical reaction and obtains the relation,

$$\frac{d \log K_v}{dT} = \frac{\bar{E} - \bar{E}}{KT^2}$$

where \bar{E} is the average energy before activation of those molecules only which pick up radiant energy and react and \bar{E} the average energy of all the molecules. In a large number of cases $\bar{E} - \bar{E}$ is zero and the temperature co-efficient is unity. In these reactions obviously $\bar{E} - \bar{E}$ has a large positive value, thus accounting for a large temperature co-efficients observed.

Application of Einstein's Law of Photochemical Equivalence.

Noddak (*Z. Electro-chem.*, 1921, 27, 360) finds that in reaction between bromine vapour and cyclohexane Einstein's law of photochemical equivalence holds good. The large temperature co-efficient observed rules out that possibility in the present case. With the aid of the available data it is possible to calculate roughly the ratio of the number of molecules that enter into photochemical reaction and the number of quanta of radiant energy absorbed. The radio-micrometer was calibrated by means of a Hefner lamp which according to Gerlach (*Physik. Zeit.*, 1913, 14, 577) radiates 900 ergs per sec. on a surface of one sq. cm. at a distance of one metre. It was found that one erg per one sq. cm. produces a deflection of 1.22 mm. in the radio-micrometer. Noddak takes $470\mu\mu$ as the mean wavelength of light absorbed by bromine.

From Table II it is evident that the number of gm. mols. of bromine transformed is .00468 in 35 minutes. So the amount transformed per sec. per sq. cm. \times depth of reaction vessel (2.5 cm.) is

$$\frac{.00468 \times 2.5}{35 \times 60 \times 1000} \text{ or } 5.56 \times 10^{-10} \text{ mols.}$$

$$\text{or } 55.6 \times 10^{-10} \text{ mols.}$$

No. of quanta absorbed

$$\frac{230 \times \frac{1}{1.22} \left(1 - 10^{-1.78 \times 2.5^* \times .01823} \right) \times 470 \times 10^{-10}}{6.07 \times 10^{23} \times 6.5 \times 10^{-17} \times 3 \times 10^{10}} = .128 \times 10^{-10}$$

* 2.5 cm. is the depth of the reaction vessel.

It thus appears that one quantum of energy at 26° leads to the formation of 436 molecules of dibromocinnamic acid. In the case of stilbene the number of molecules of the dibromo derivative formed per quantum of energy at 26° comes out to be 305. Eggert (*Physik. Zeit.*, 1924, 25, 19) finds that in the transformation of maleic ester to fumaric ester by bromine under the influence of light, the number of molecules transformed per quantum absorbed is 565. Nernst (*Z. Electro-chem.*, 1918, 24, 335) considers that similar high values by Bodenstien and Dux (*Z. physikal. Chem.*, 1923, 85, 297) in the combination of hydrogen and chlorine are due to a primary photochemical reaction being followed by secondary ones. There are no facts available which would justify the assumption that the above explanation of Nernst holds good in the reactions stated here.

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The Phenomenon of After-effect in certain Photochemical Reactions.

BY

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In previous papers (Dhar, *Z. anorg. Chem.*, 1922, 121, 1561; *J. Chem. Soc.*, 1923, 123, 1856) it has been mentioned that the reaction between potassium oxalate and iodine is very sensitive to light. We have observed that a mixture of potassium oxalate and iodine when exposed to light and brought back to darkness shows a greater velocity in the dark than when the reacting mixture is not at all exposed to light. This phenomenon is known as "after-effect" in photochemical reactions.

The phenomenon of "after-effect" has already been noted in certain photochemical changes. In solvents other than alcohol the oxidation of iodoform as studied by Plotnikow (*Z. physikal. Chem.*, 1911, 76, 743) shows a marked after-effect when illumination has ceased. Trautz and Thomas (*Physik. Z.*, 1906, 7, 899; *Z. Elektrochem.*, 1907, 13, 550; *Z. Wiss. Phot.*, 1906, 4, 352) note after-effect of illumination in the photo-oxidation of sodium sulphide, of cuprous chloride in hydrochloric acid solution and of benzaldehyde. That the benzaldehyde oxidation shows an after-effect when illumination has been discontinued has been confirmed by Bäckström (Taylor's *Physical Chemistry*, p. 1247). Kistiakowsky (*Z. physikal.*

Chem., 1900, 35, 431) observed an after-effect of illumination in the case of the photo-decomposition of hydrogen peroxide by visible light in presence of ferro- and ferricyanides.

With a view to test whether any after-effect of illumination takes place or not in photo-sensitive reactions we investigated a number of reactions in aqueous solutions. Some of these reactions are known to be markedly photo-sensitive either to visible or to ultra-violet light while others are only moderately so.

EXPERIMENTAL.

The experiments were carried out as follows: A 500 c.p. Point-o-lite lamp was used as the source of illumination. The reactions took place in a beaker which was placed at a measured distance apart from the source of light. The light was switched on as soon as the reactants were mixed together and after a few minutes' exposure it was turned off. The beaker was immediately removed to complete darkness, 5 c.c. of the mixture withdrawn and the amount of change in it determined by titration. Further readings were continued to be taken by thus placing the reacting system in darkness. The reacting mixtures were again mixed together in a beaker identically as before but this time instead of exposing the system to the Point-o-lite lamp for the first few minutes it was kept all along in the dark and readings taken at intervals.

The following experimental results are obtained and they are of a preliminary nature. The unimolecular coefficients have always been calculated from the beginning of the reactions.

TABLE I

*Potassium Oxalate and Iodine at 32° C.**N/10-Potassium Oxalate and N/137-Iodine.*

Distance from the source of light = 21 cm.

Exposed to light for 5 minutes and then removed to darkness			In the dark throughout		
t (minutes)	$a-x$ (c.c.)	k_1 (unimolecular)	t (minutes)	$a-x$ (c.c.)	k_1 (unimolecular)
0	7.3	0	7.3
5	6.5	.0101	7.5	6.7	.00496
15	5.75	.00691	20	5.9	.00462
30	4.65	.00653	40	4.65	.00489
Mean =		.00672	Mean =		.00482

TABLE II

*Tartaric Acid and Bromine at 32° C.**N/10-Tartaric acid and N/111.2-Bromine.*

Distance from the Point-o-lite lamp = 21 cm.

Exposed to light for 5 minutes and then removed to darkness			In the dark throughout		
t	$a-x$	k_1	t	$a-x$	k_1
0	9.0	0	9.0
5	8.9	.0726	5	7.8	.0124
7					
12	2.5	.0464	12	6.7	.0107
20	1.0	.0477	20	4.1	.0171
Mean =		.0471	Mean =		.0134

TABLE III

*Lactic Acid and Bromine at 32° C.**N/10-Lactic acid and N/125-Bromine.*

Distance from the Point-o-lite lamp = 21 cm.

Exposed to light for 5 minutes and then removed to darkness			In the dark throughout		
<i>t</i>	<i>a—x</i>	<i>k₁</i>	<i>t</i>	<i>a—x</i>	<i>k₁</i>
0	8·0	0	8·0
5	4·35	·0529	6	6·4	·0162
12	2·7	·0393	15	4·1	·0194
20	1·5	·0364	30	1·8	·0216
Mean = ·0379			Mean = ·0191		

TABLE IV

*Malic Acid and Bromine at 32° C.**N/10-Malic acid and N/125-Bromine.*

Distance from the Point-o-lite lamp = 21 cm.

Exposed to light for 5 minutes and then removed to darkness			In the dark throughout		
<i>t</i>	<i>a—x</i>	<i>k₁</i>	<i>t</i>	<i>a—x</i>	<i>k₁</i>
0	8·0	0	8·0
5	3·35	·0756	5	6·0	·0249
12	2·3	·0451	12	4·5	·0209
18	1·4	·0421	25	2·2	·0224
Mean = ·0436			Mean = ·0227		

TABLE V

Oxalic Acid and Bromine at 32° C.

*N/10-Oxalic acid and N/111·2-Bromine.
Distance from the Point-o-lite lamp = 27 cm.*

Exposed to light for 5 minutes and then removed to darkness			In the dark throughout		
<i>t</i>	<i>a—x</i>	<i>k₁</i>	<i>t</i>	<i>a—x</i>	<i>k₁</i>
0	9·0	0	9·0
5	1·9	·1351	6	3·3	·0726
12	0·75	·0899	12	1·3	·0702
20	0·2	·0628	20	0·45	·0651
Mean = ·0864			Mean = ·0693		

TABLE VI

Citric Acid and Bromine at 32° C.

*N/10-Citric acid and N/136-Bromine.
Distance from the Point-o-lite lamp = 21 cm.*

Exposed to light for 5 minutes and then removed to darkness			In the dark throughout		
<i>t</i>	<i>a—x</i>	<i>k₁</i>	<i>t</i>	<i>a—x</i>	<i>k₁</i>
0	8·4	0	8·4
5	6·25	·0257	9½	5·8	·0171
15	4·2	·0202	20	3·75	·0175
30	2·3	·0188	35	2·0	·0170
Mean = ·0195			Mean = ·0172		

TABLE VII

Potassium Formate and Iodine at 32° C.

*N/6·4-Potassium formate and N/100-Iodine.
Distance from the Point-o-lite lamp = 21 cm.*

Exposed to light for 5 minutes and then removed to darkness			In the dark throughout		
<i>t</i>	<i>a-x</i>	<i>k₁</i>	<i>t</i>	<i>a-x</i>	<i>k₁</i>
0	10·0	0	10·0
5	7·0	·0309	5	7·9	·0205
12	5·6	·0209	12	5·8	·0200
20	3·6	·0222	20	3·9	·0205
Mean = ·0216			Mean = ·0203		

TABLE VIII

Sodium Citrate and Iodine at 32° C.

*N/11·6-Sodium citrate and N/137-Iodine.
Distance from the Point-o-lite lamp = 21 cm.*

Exposed to light for 5 minutes and then removed to darkness			In the dark throughout		
<i>t</i>	<i>a-x</i>	<i>k₁</i>	<i>t</i>	<i>a-x</i>	<i>k₁</i>
0	7·3	0	7·3
5	5·8	·0200	8	6·3	·00800
15	5·1	·0104	25	5·1	·00628
30	4·4	·00738	45	3·7	·00655
Mean = ·00886			Mean = ·00698		

TABLE IX

Oxalic Acid, Chromic Acid, Manganous Sulphate and Sulphuric Acid at 32° C.

N/30-Oxalic acid, N/517·2-Chromic acid, N/11·4-Sulphuric acid, N/600-Manganous sulphate.

Distance from the Point-o-lite lamp = 21 cm.

Exposed to light for 3 minutes and then removed to darkness			In the dark throughout		
<i>t</i>	<i>a-x</i>	$k_o = x/t$	<i>t</i>	<i>a-x</i>	$k_o = x/t$
0	9·3	0	9·3
3	7·8	·50	3½	8·05	·36
8	6·05	·41	8	6·5	·35
12½	3·3	·47	13	4·7	·35
Mean = 0·44			Mean = 0·353		

TABLE X

Oxalic Acid, Potassium Permanganate, Manganous Sulphate and Sulphuric Acid at 32° C.

N/30-Oxalic acid, N/506·4-Potassium permanganate, N/600-Manganous sulphate and N/11·4-Sulphuric acid.

Distance from the Point-o-lite lamp = 21 cm.

Exposed to light for 45 seconds and then removed to darkness			In the dark throughout		
<i>t</i>	<i>a-x</i>	k_1	<i>t</i>	<i>a-x</i>	k_1
0	7·95	0	7·95
½	5·5	·210	1½	4·1	·192
1½	4·2	·185	3	2·35	·176
8	3·2	·180	4	2·1	·145
Mean = ·183			Mean = ·171		

TABLE XI

Potassium Persulphate and Potassium Iodide at 32°.

N/12-Potassium iodide and N/100-Potassium persulphate exposed to moderately bright sunlight.

Exposed to sunlight for 1 minute and then removed to darkness			In the dark throughout		
t	$a-x$	$k_0 = x/t$	t	$a-x$	$k_0 = x/t$
0	0	0	0
1	2.4	2.4	1½	2.5	1.687
3½	6.2	1.807	4½	7.2	1.694
.5	9.4	1.880	6	10.2	1.70
Mean = 1.894			Mean = 1.687		

It is well known that the reaction between ferric chloride and ammonium oxalate is very sensitive to sun-light so this reaction, too, was studied to test if there existed any after-effect of illumination. Some ferric chloride, a larger quantity of ammonium oxalate and a few crystals of oxalic acid were mixed together and divided into two portions. One portion was exposed to bright sunlight while the other was kept in total darkness. The portion exposed to the sun began to show a precipitate of ferrous oxalate in about 10 minutes. As soon as the precipitate began to come out, the solution was removed to a dark room and filtered through double filter paper. The clean filtrate was now kept in total darkness and in about half-an-hour quite a large amount of precipitate was noted in this filtrate. The other portion of the original mixture which had been kept in the dark showed no formation of precipitate even after a much longer period.

It is evident that all the reactions investigated above are accelerated to a certain extent by the light from a Point-o-lite lamp and it is to be observed that all these light-sensitive reactions when once exposed to the light

for the first few moments proceed (in the absence of the light) with an appreciably greater velocity than in the case when the reactions take place all along in the dark. It should be noted that the foregoing results are only of a comparative nature.

The following figures will show the amount of acceleration caused by the light as well as the corresponding increase in the velocity of the reactions after the Point-o-lite lamp has ceased to work over the velocity of the reactions proceeding all along in the dark.

TABLE XII

Reaction	Acceleration in the velo- city produced by light	Ratio of the velocity of the dark reaction after the light has ceased to work to the velocity of the reaction in the dark all along
Tartaric acid and Bromine (Table II)	5·4 times	$\frac{.047}{.013} = 3\cdot7$
Lactic acid and Bromine (Table III)	3·2 "	$\frac{.038}{.019} = 2\cdot0$
Malic acid and Bromine (Table IV)	3·2 "	$\frac{.044}{.023} = 1\cdot95$
Sodium citrate and Iodine (Table VIII)	2·9 "	$\frac{.0089}{.0069} = 1\cdot3$
Potassium oxalate and Iodine (Table I)	2·1 "	$\frac{.0067}{.0048} = 1\cdot4$
Oxalic acid and Bromine (Table V)	1·9 "	$\frac{.087}{.070} = 1\cdot2$
Citric acid and Bromine (Table VI)	1·5 "	$\frac{.019}{.017} = 1\cdot1$
Potassium formate and Iodine (Table VII)	1·5 "	$\frac{.022}{.020} = 1\cdot1$
Oxalic acid, Chromic acid, Manganese sulphate and Sulphuric acid (Table IX).	1·43 "	$\frac{.44}{.35} = 1\cdot23$
Potassium persulphate and Potassium iodide (Table XI).	1·42 "	$\frac{1\cdot90}{1\cdot69} = 1\cdot18$
Oxalic acid, Potassium permanganate, Manganese sulphate and Sulphuric acid (Table X).	1·2 "	$\frac{.183}{.171} = 1\cdot07$

From the above table it is at once evident that there exists a proportionality between the ratio of the velocity of a reaction in the dark after the light has ceased to work to the velocity of the reaction throughout in the dark and the corresponding acceleration of the velocity of the reaction by the light. In other words, the greater the acceleration caused by the light the greater is the after-effect produced in the reaction.

Among the reactions investigated by us we observed a few cases, which, in spite of being markedly photo-sensitive, exhibit no after-effect. The reaction between sodium potassium tartrate and bromine is accelerated by light yet the ratio of the velocity of the reaction in the dark after the light has ceased to work to the velocity in the dark all along remains almost unity. A mixture of mercuric chloride and ammonium oxalate was exposed to sunlight and just when some calomel began to form, it was filtered off and the filtrate kept in a dark room. No further precipitation of calomel took place in the filtrate in the dark. Again the decompositions of Fehling's solution and a mixture of an oxalate and copper sulphate solution take place readily in strong sunlight, and deposit of copper is obtained but in none of these cases any after-effect was observed after illumination.

It is very difficult to explain the after-effect in photochemical reactions and no satisfactory suggestion in explaining this phenomenon has yet been advanced.

We shall cite certain facts which are more or less allied to these photochemical after-effects. Phillips (*Proc. Roy. Soc.*, 1913, 89, 42) exposed mercury vapour in a quartz tube to radiations containing $\lambda = 2537\text{\AA}$ from a mercury lamp. He found that the mercury vapour began to fluoresce and he observed that the glow passed up the tube and spread out to a distance of 18 inches from the place of illumination.

In a previous paper (*Z. anorg. Chem.*, 1924, 141, 1) we have suggested the explanation of this observation of Phillips in the following way:—

The atoms of mercury in the mercury vapour become activated by the absorption of light $\lambda=2537\text{\AA}$. The activated atoms in losing the extra amount of energy can give out radiation and can emit the glow. Now, the activated atom in coming in contact with an inactive atom which has not been illuminated can impart its energy to the inactive atom and activate it. This process can repeat itself and a long column of mercury vapour becomes activated and gives a glow though not illuminated. Though the life period of an activated atom or molecule is of the order 10^{-8} second it seems probable that by these collisions the glow can continue to a much longer period.

It was observed originally by Stark (*Ann. Phys.*, 1904, 14, 520) that a stream of mercury vapour, allowed to distil away from the arc or glow discharge in vacuo, remains luminous. It may be said to carry the luminosity away with it and in the case of the arc discharge there is no difficulty in detecting the luminosity for 50 cm. or so from the source.

Lord Rayleigh has obtained more or less similar results (*Proc. Roy. Soc.*, 1911, A 90, 364; 1914, 91, 92; 1925, 108, 262). Consequently, there is absolutely no doubt in the fact that light persists in the vapour even after the source of excitation has been removed and this is exactly a phenomenon of the same nature as the after-effect in photochemical reactions, and we are of the opinion that the cause of both the phenomena would be identical. It seems possible in photochemical reactions that on illumination some of the molecules of the reacting substances become activated and these activated molecules by impact can activate other inactive molecules and this process is likely to take time and consequently, even when the source of

illumination is removed, the activated molecules take some time to die out and hence the chemical action persists for a short time even after the illumination is cut off.

Franck and Grotian (*Z. Physik*, 1921, 4, 89) have repeated the experiment of Phillips and have accounted for the persistence of the luminosity by supposing that the excited atoms, which have absorbed $\lambda = 2537\text{\AA}$ and are prepared to re-emit this line, unite with other mercury atoms to form molecules. When these molecules are again dissociated the stored energy can be liberated and $\lambda = 2537\text{\AA}$ is emitted.

Several years ago Weigert (*Ann. Physik*, 1907, 24, 243) threw out the suggestion that a photo-chemical change may consist in the intramolecular transformation of the molecules of the light-absorbing substance or in the formation of molecular complexes which act as reaction-nuclei under illumination. It is needless to say that there is hardly any experimental support to these conjectures. Similarly, for lack of experimental support this phenomenon of after-effect cannot be associated with the existence of chain reactions or intermediate-compound formations. That a series of frequencies is active in a chemical change is explained by Perrin (*Ann. Physique*, 1919, 11, 1; *Trans. Faraday Soc.*, 1922, 17, 547) and by Lewis (*J. Chem. Soc.*, 1922, 121, 613) by assuming that such reactions take place in steps with the formation of intermediate compounds. Though it may be true in a few cases yet in the majority of reactions the validity of this assumption cannot be experimentally proved. The very recent developments of the "activation theory" seem to do away with the necessity of such arguments.

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Note on the Permeability of Membranes.

BY

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Some years ago Barlow (*Phil. Mag.*, (6), 10, 1; 1906, 11, 595) showed that the presence of alcohol made a copper ferrocyanide membrane permeable to sugar, though no explanation was given. In a recent paper, Bancroft and Gurchot (*J. Phys. Chem.*, 1924, 28, 1279) have explained this fact on the assumption that alcohol coagulates the membrane, thus making it permeable to sugar. "Since sugar is insoluble in alcohol, it is clear that the alcohol cannot make the copper ferrocyanide membrane permeable to sugar by increasing the solubility of the sugar in the membrane. There must therefore have been a fundamental change."

Less than two per cent. of methyl alcohol was sufficient to make the copper ferrocyanide membrane permeable to sugar. With the higher alcohols the necessary concentrations were much lower. A forty per cent. methyl alcohol coagulated a solution of copper ferrocyanide, and the authors consider that the precipitation of the solution is a much less sensitive test than the one for the permeability of the membrane, though it supports their explanation.

In a recent paper (Sen, *J. Phys. Chem.*, 1925, 28, 517) a study has been made on the stability of copper ferrocyanide sol, and it was found that alcohol could not coagulate the sol in the absence of electrolytes under the experimental conditions. I have therefore made some more experiments with a freshly prepared and concentrated sol of copper ferrocyanide with a view to study under

what conditions colloidal copper ferrocyanide is precipitated by alcohols. I shall only summarise the results obtained by me.

(1) Colloidal copper ferrocyanide can be precipitated by means of alcohols in presence of small quantities of electrolytes. The purer the sol the greater is its stability towards alcohols.

(2) A concentrated sol can be coagulated more easily than a dilute sol. Ethyl alcohol in a concentration of sixty per cent. coagulated the sol in one hour whereas with a half-diluted sample of the same sol no sign of coagulation was visible even after seventy hours.

(3) With methyl, ethyl, propyl and butyl alcohols, the higher the alcohol, the greater is the precipitating power.

These results therefore support the views of Bancroft and Gurchot. In my previous paper a dilute sol was used and the coagulation time was only two hours with the alcohols. Further the concentrations of the alcohols added were never high. Hence no coagulation of the sol was observed. The results of this paper further show that the highly concentrated membranes of copper ferrocyanide should be more sensitive to alcohols than the dilute ones. It is also probable, as Tinker (*Proc. Roy. Soc.*, 1916, 92, 364) has shown, that stable membranes always contain traces of either copper sulphate or potassium sulphate, which means a sensitisation in presence of alcohols. Greater sensitiveness to higher alcohols is also explained by my results, as they have greater coagulating action.

Though this simple and interesting explanation of Bancroft and Gurchot has been supported by my qualitative experiments, there is an apparent difficulty in extending this to some other cases. Thus Traube (*Archiv. Anat. Physiol. und Wissenschaft. Medizin*, pp. 87-165, 1867) showed that copper ferrocyanide is not permeable to either

of the solutions from which it is formed, nor to barium chloride, calcium chloride, ammonium sulphate, barium nitrate, sugar, etc.; it is, however, permeable to potassium chloride. There is no reason why salts of barium or calcium should not be permeable, for these salts are powerful precipitants of the copper ferrocyanide membranes, unless it is assumed that they were used in very dilute solutions in which case complete adsorption of the cations took place by the negative membrane (Frankert and Wilkinson, *J. Phys. Chem.*, 1924, 28, 651). The membrane ought to be permeable to moderate concentrations of barium chloride, unless, however, the charge on the membrane be reversed in which case negative osmosis shall occur, because negative osmosis is dependent on the electrical polarisation of the capillaries of the membranes, and this polarisation is brought about by ionic adsorption, (*cf.* Bartell *J. Am. Chem. Soc.*, 1914, 36, 646; Bartell and Hocker, *ibid.*, 1916, 38, 1029, 1036; Bartell and Madison, *J. Phys. Chem.*, 1920, 24, 593). Potassium chloride may not be permable depending on the amount of its adsorption, for selective adsorption has an important part to play in the permeability of substances, but this side of the problem is in a very unsatisfactory state.*

Lastly, it may be said that the proofs given in the paper of Bancroft and Gurchot and in this one as regards the coagulation points of view are of indirect nature. A direct method would be to utilise Tinker's methods (*loc. cit.*) and get some microphotographs of copper ferro-

* In this connection it may be stated that H. N. Morse has reported that changes of structure take place when a copper ferrocyanide membrane is bathed by various aqueous salt solutions. They also take place with zinc ferrocyanide and manganese ferrocyanide even in water (*Report on Osmotic Pressure of Aqueous Solutions*, Chaps. IV and XI, Carnegie Institute of Washington, 1914).

cyanide and other membranes with drops of dilute alcohol and other acids added to them. The results would show definitely whether we are getting coagulation or not in these cases.

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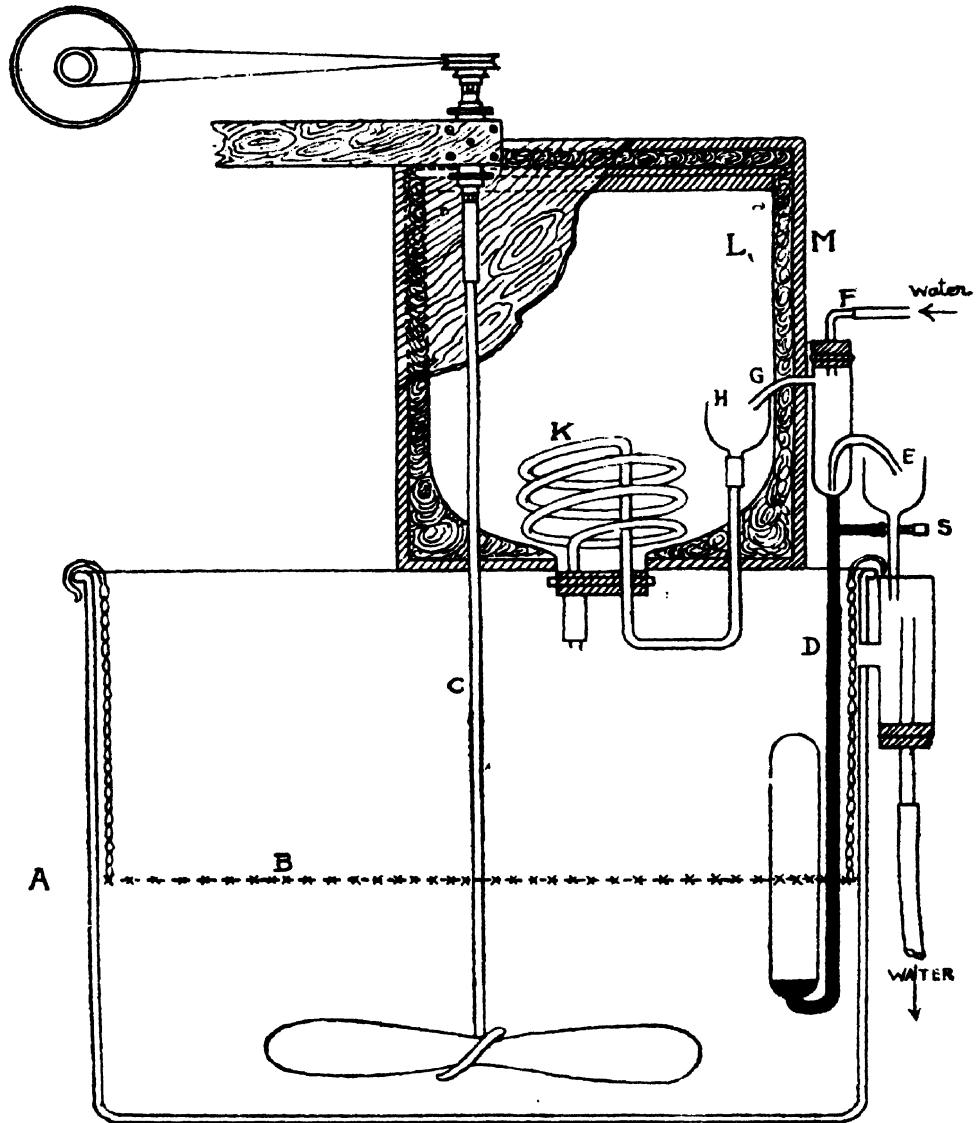
A Note on an Improved Device for Working a Thermostat at Low Temperatures.

BY

C. J. J. FOX AND C. L. MANKODI.

The general practice in physical chemistry is to take standard measurements at 18°C or 25°C. At Bombay the temperature of the atmosphere rarely falls below 25°C and the necessity is felt of fitting up a thermostat which would work conveniently and smoothly at 25°C.

Foote (*Z. physical. Chem.*, 1900, 33, 740) has described a thermo-regulator suitable for running a thermostat at low temperatures. The thermo-regulator is filled with toluene and mercury as the ordinary gas thermo-regulator. The head of the regulator *D* contains an inlet tube *F*, and two exit tubes *E* and *G*. The method of its working, as suggested by Foote, is to admit ice-cold water continuously into the regulator by the tube *F*. When the temperature of the thermostat rises, above the one required, ice-cold water entering the regulator by the tube *F* falls out from the tube *G* into the thermostat and thus lowers the temperature of the thermostat. But



when the thermostat maintains the required temperature or any temperature lower than that, water entering the thermo-regulator by the tube *F* flows out from the tube *E* to the sink. In this way a large amount of ice is consumed and is simply wasted when the thermostat runs satisfactorily.

Hickman (*J. Chem. Soc.*, 1923, 123, 3416) has also described a modified form of an arrangement for running a thermostat at low temperatures. The thermo-regulator used by him is almost of the same type as Foote's regulator but instead of passing ice-cold water continuously through the regulator he allows water at ordinary temperature to flow through it. When the temperature of the thermostat rises, this water flows out from an exit into a water-bath packed with ice, where it gets cooled, and then falls into a spiral placed in the thermostat. The spiral gets cooled and consequently the temperature of the thermostat is lowered. This method does not, as the previous one, involve the running of the ice-cold water to waste but the position of the spiral in the thermostat is not desirable because it interferes with the stirring and does not leave sufficient accommodation for other apparatus to be placed in the thermostat.

The device, which is described in the following note, avoids the waste of ice-cold water and also requires a much simpler fitting. Hickman's auxiliary water-bath has been totally dispensed with and the spiral is kept outside the thermostat and thus more space inside the thermostat is rendered available.

The thermo-regulator *D* is of the same pattern as the one used by Foote (*loc. cit.*). Water at ordinary temperature enters the thermo-regulator continuously by the tube *F* and when the temperature of the thermostat is at or below 25°C it flows out by the tube *E* to the sink. When the thermostat rises in temperature, water instead,

of directly flowing out from the tube *G* into the thermostat (as in Foote's method) falls into the funnel *H*, whence it is conveyed first to a spiral *K* immersed in crushed ice. Water when passing through the spiral gets cooled and flows out by the other end of the spiral into the thermostat and thus adjusts the temperature.

To work this arrangement satisfactorily, it is very important that the two water exits *E* and *G* from the thermo-regulator should not have rubber tubing attached to them to carry away water but should empty directly into open funnels. In this way all siphoning action is avoided and the thermo-regulator is made more uniform in its action because there is no risk of any drop of mercury being siphoned away with water and hence no disturbance in the adjusted column of mercury takes place. This arrangement requires, of course, that the top of the spiral *K* should be a shade lower than the water level attainable in the funnel *H*. The exit end of the spiral *K* is covered with a piece of thick-walled rubber tubing to act as lagging. The glass vessel *L* which holds the crushed ice is packed with wool in the wooden box *M* and the thermostat *A* is also wrapped around with cotton wool (not shown in the figure). *B* is a platform made of brass-wire netting which can be raised or lowered by brass chains. The stirrer *C* is made of glass tubing (the brass tubing would be more robust, of course) which is fastened to the hub of a bicycle wheel through a short sleeve made of brass tubing into which it is fastened with sealing-wax. The hub of a bicycle wheel is excellent for this purpose because its spindle rotates on ball bearing and hence avoids all contact friction. The cork through which the ends of the spiral *K* pass has also a third outlet (not shown in the figure) which can be opened when water from the vessel *L* has to be run out. *S* is a screw to adjust the exact quantity of mercury

required in the thermo-regulator for any particular temperature.

With the modifications described above, it was found that in Bombay when the air temperature was about 30°C the thermostat holding about 40—50 gallons of water could be kept running steadily at temperature $25^{\circ} \pm 0.03$ throughout the day with a consumption of not more than 10-15 lbs. of ice and without requiring any attention whatever.

If the air temperature happens to fall below 25°C a very small flame kept below the thermostat adjusts the temperature without requiring any other alteration in the arrangement.

When the thermostat is to be used to maintain a constant temperature which is much below the room temperature, radiation from the sides of the thermostat will be great and the working of the thermostat will not be as satisfactory as at 25°C or as at any temperature which is lower but near the room temperature. It will, however, be possible to use the thermostat to maintain constant temperatures even when the temperatures are not very near the room temperature by reducing the radiation from the sides to a minimum and maintaining an adequate supply of ice-cold water. The top of the thermostat in such instances will, of course, have to be covered with a lid of some non-conducting material.

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BOMBAY,

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Variation of the Charge of Colloidal Particles with Concentrations of Electrolytes.

Part I.

Arsenious Sulphide Sol and Acids

Br

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AND

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The stability of most colloidal solutions of inorganic substances is intimately connected with its electric charge. We believe that the potential of the double layer is one out of several factors which determine the rate of precipitation (*cf.* Mukherjee and Sen, *J. Chem. Soc.*, 1919, 115, 466; Mukherjee, *ibid.*, 1920, 117, 356; and Papaconstantinou, *ibid.*, 1920, 117, 1566; Mukherjee and Majumdar, *ibid.*, 1924, 125, 791). One of us has suggested that the narrowness of the range of precipitating concentrations is to be sought for in the great effect, which a small diminution of the potential of the double layer has on the percentage of successful collisions between the particles, which lead to their coalescence (Mukherjee, *Thesis*, 1921, also Mukherjee and Majumdar, *loc. cit.*). When two particles come near each other, the mutual electrical forces disturb the distribution of the ions composing the mobile sheet of the double layer and a new arrangement results. The displacement of these ions that takes place requires the expenditure of work against electrical forces at the expense of the kinetic energy of approach of the colliding particles. The stabilising effect of the electrical double

layer is to be attributed to this energy change. It is well-known that cohesive forces decrease much more rapidly with distance than electrical forces and it is only when the particles are sufficiently near each other that they predominate over the electrical forces. The fraction of the total number of collisions which is successful in bringing about coalescence, would therefore be dependent on the magnitude of the cohesive forces¹ and on the change in the electrical energy associated with such coalescence. *The electrical work will evidently depend on the number of ions which suffer a shift in their position, on the changes in their positions with respect to the colloidal particles and on the dielectric constant of the medium.* The number of displaceable charges determines the density of the free electrical charge of the colloidal particle. Thus we see that other things remaining unaltered, as the free charge on the surface of the colloid decreases the electrical work referred to above also diminishes. Though investigations on the coagulation of colloids under different conditions are numerous, determinations of electrical charge under these conditions are seldom made. In most papers in discussing the experimental results, one or more of the following assumptions are usually made:—

- (1) The electrical charge of the colloid does not vary on dilution. If there is a diminution of the charge with dilution, the discussion of results and the conclusions drawn therefrom lose much of their force, and in some cases they are to be completely revised (*cf. Mukherjee and Chaudhuri, J. Chem. Soc., 1924, 125, 801*).
- (2) Coagulation takes place at the iso-electric point.

¹ It is also quite possible that when the particles are not exactly spherical, relative positions of the two particles might mean a difference in the magnitude of the cohesive forces, which are brought into play.

(3) The electrical charge (or the potential of the double layer) on the particles of a colloid is identical for concentrations of different electrolytes which produce the same rate of coagulation.

No data are, however, given to support such assumptions. The absence of such determinations is in part to be ascribed to the difficulties in making reliable and accurate determinations of the charge. In the present paper the data obtained on the influence of acids on the electrical charge of arsenious sulphide hydrosols prepared under different conditions are recorded, and the results have been discussed from the theoretical point of view.

EXPERIMENTAL.

A.—*Method of Measuring the Charge.*

The method, described by one of us (Mukherjee, *Proc. Roy. Soc.*, 1923, 103, 102), has been found to give reliable and accurate values for the velocity of migration. *What we actually measure is the velocity of the colloidal particles under unit potential gradient.* Without further assumptions it is not possible to assign a definite value either to the electric charge on the particles or the potential of the double layer surrounding them. A variation in the velocity may be taken to indicate a proportionate variation in the density of the electrical charge (*cf.* Lamb, Smoluchowski, *vide supra*). The apparatus, previously described, has been slightly modified. The distance between the side tubes has been increased to 2 cm. In course of the large number of measurements we have made, we had occasion to examine more closely other sources of error which were not referred to in the earlier paper (Mukherjee, *loc. cit.*). We have found that the heating effect of the electric current is negligible unless the potential gradient and the specific conductivity of

the liquid are very great. The viscosity of the medium in which the particle moves ought to be measured. In the present instance the variations in viscosity are negligible compared to the error involved in reading the movement of the boundary. Electrolysis during the measurement is a greater source of error and care ought to be taken to use not very high potential gradients or prolong the movement too long. *It is of utmost importance to determine the potential gradient before and after the movement and to secure a minimum variation in its value.* For in case of large changes in the potential gradient during the movement, there is an obvious error in calculating the velocity per unit potential gradient unless we also know accurately the variation in the potential gradient continuously with time during the movement of the boundary. For these reasons we do not think it desirable to simplify the procedure as has been done by Freundlich and Zeh (*Z. physical. Chem.*, 1924, 114, 65).

B.—*Preparation of Arsenious Sulphide Sols.*

The sols were prepared in several ways as follows:

(1) Equal volumes of water saturated with hydrogen sulphide and doubly diluted saturated solution of arsenious acid were mixed. The resulting mixture was divided into two portions. Through one portion pure hydrogen sulphide was bubbled for one hour (sol A). Through the other portion pure hydrogen was passed till there was no smell of the sulphuretted hydrogen, *i.e.*, into this portion, hydrogen sulphide was not passed at all after the mixing (sol B). A portion of sol B was coagulated and when hydrogen sulphide was passed into the clear decanted liquid, arsenious sulphide was precipitated, showing the presence of free arsenious acid in the sol. The results with these sols are given in Table I.

(2) The colloid was prepared by mixing equal volumes of water saturated with hydrogen sulphide and doubly diluted saturated solution of arsenious acid, and then by passing hydrogen sulphide to saturation. The hydrogen sulphide was then driven off by pure hydrogen (sol C). A portion of this colloid was taken and saturated with hydrogen sulphide when required on the day of the experiment. The water or the acid used was also saturated with hydrogen sulphide (sol D). The results are given in Table II. The results with H_2SO_4 were obtained with a different sol prepared as in the case of sol C (sol C').

(3) Equal volumes of water saturated with hydrogen sulphide and 4 times diluted saturated solution of arsenious acid were quickly mixed and thoroughly shaken and hydrogen sulphide and then hydrogen were passed as usual (sol E). The results are given in Table III.

In the following tables v , stands for the velocity of migration of the colloid-electrolyte boundary in cm. per sec. per volt per cm.; C , stands for concentration of the electrolyte in gm. equivalents per litre and C_H ,* for hydrogen ion concentration at 18° .

TABLE I

Arsenious Sulphide Sol and Hydrochloric Acid.

Concentration (C)	Rate of migration (v)	
	Sol A	Sol B
0	48.6	62.9
0.00038	52.0	—
0.001	56.1	54.0
0.002	51.7	47.0
0.004	52.5	45.0
0.01	58.1	44.3

* Calculations of hydrogen ion concentrations of the weak acids have been made from data on conductivity (vide Kohlrausch, *Leitvermögen der Elektrolyte*).

TABLE II
Arsenious Sulphide.

Concentration (<i>C</i>)	Rate of migration (<i>v</i>)		
	Sol C' and HCl	Sol D and HCl	Sol C' and H ₂ SO ₄
0	53.2	59.4	71.8
0.00033	44.3	52.3	60.9
0.00066	—	—	57.0
0.001	41.7	48.8	—
0.002	45.1	48.5	—
0.004	45.9	42.8	54.5

DISCUSSION OF RESULTS.

A.—Irregular Variation of the Charge with Acids.

It will be seen from Table I that sol A shows a complicated variation of the velocity with the concentration, whereas a simpler variation was observed with sol B. Sol B differed from sol A in being free from hydrogen sulphide and also contained an appreciable quantity of free arsenious acid. Freundlich and Nathansohn (*Koll. Zeit.*, 1921, 28, 258) have suggested that the free hydrogen sulphide present in arsenious sulphide sols is photochemically oxidised to sulphur dioxide, which again reacts with hydrogen sulphide to form pentathionic acid and sulphur. This sulphur adsorbs polythionate ions and thus passes into the colloidal state. In a recent paper Murphy and Mathews (*J. Am. Chem. Soc.*, 1923, 45, 16) mention that the assumption of the presence of polythionic acids is necessary to explain the increase in conductivity of the sol on exposure to light. Bhatnagar and Lakshan Rao have also shown in an interesting study (*Koll. Zeit.*, 1923, 33, 164) that the transformation of the colour of orange sols of arsenious sulphide into yellow is due to the oxidation of the particles.

It may therefore be suggested that the observed complicated nature of the variation in the charge in the presence of free H₂S might be the result of several complicated reactions, namely,

(1) Interaction between hydrogen ions and anions of polythionic acids and of hydrogen sulphide in the adsorbed layer and in the solution.

(2) The change in the composition of the colloidal particles due to the formation of sulphur by reaction between polythionate ions and hydrogen ions.

We would like to draw attention to the results with sol D which shows a simpler variation. Here hydrogen sulphide was passed into the sol on the day of the experiment. It seems probable, therefore, that the mere presence of hydrogen sulphide does not produce the above-mentioned complicated variation in the charge. The sols which show a complicated variation are those which have remained in contact with hydrogen sulphide for sometime. On the other hand, sols containing free arsenious acids or which have been in contact with hydrogen sulphide for a short interval of time (12 hours), show a much simpler behaviour. We are, therefore, inclined to believe that the complicated behaviour is due to interaction between hydrogen ions and anions of polythionic acids and that the anions of hydrogen sulphide are not responsible for it. The effect of time is also intelligible as the formation of polythionic acids from the oxidation of hydrogen sulphide in solution requires time. *We would therefore conclude that sols formed in a medium containing arsenious acid in excess owe their charge practically to the adsorption of the anions of hydrogen sulphide, whereas the charge on the others is the result of the primary adsorption of anions of hydrogen sulphide and probably also of the anions of polythionic acids.*

B.—Comparison of different Acids regarding their Effect on the Charge.

Since the presence of free hydrogen sulphide would lead to the formation of thionic acids (and of sulphur) which, as we have just seen, would react with hydrogen ions, it was decided to compare the effect of different acids on the sols whose particles had a simpler composition. Sol E shows a simpler variation of the charge with the concentration of acid. It was prepared under conditions so that there was an excess of arsenious acid. In our previous work most of the experiments on coagulation were carried on with such sols.

TABLE III

Sol E.

Hydrochloric acid			Oxalic acid			Formic acid		
C	v	c _H	C	v	c _H	C	v	c _H
0	68.0	—	0	68.0	—	0	68.0	—
0.005	52.6	0.0048	0.033	47.5	0.0122	0.02	45.2	0.00244
0.02	45.4	0.019	0.05	41.8	0.0175	0.05	42.2	0.00305
0.025	45.8	0.024	0.083	38.6	0.0265	0.066	37.9	0.0046
0.033	45.0	0.031	0.111	36.3	0.0333	0.443	37.2	—
						2.46	34.7	0.027

SOL E AND ACETIC ACID.

C	v	c _H
0	68.0	—
0.011	51.3	0.00045
0.1	35.7	0.0013

It is rather unexpected to observe in Table III that acetic and formic acids at the same hydrogen ion concentration have lowered the rate of migration, that is, the density of the electrical charge, to a greater extent than hydrochloric and oxalic acids.

Mukherjee and Chaudhuri found that a concentration of 10 normal acetic acid fails to coagulate arsenious sulphide sols. Freundlich (*Kapillarchemie*, 1922) has pointed out that the lower coagulating power of salts of organic acids is to be attributed to the adsorption of anions. One would expect that on account of the adsorption of anions in presence of acetic acid, the negative electrical charge will have a greater value than in the presence of hydrochloric acid of the same hydrogen ion concentration. The fact that acetic acid fails to coagulate arsenious sulphide sols *apparently* seems to confirm this conclusion. But the actual facts completely contradict this interpretation. We see that, contrary to our expectations, acetic acid has a greater capacity to diminish the charge than hydrochloric acid. Obviously the rate of migration alone does not determine the rate of coagulation. Apart from the relationship between the charge and the rate of coagulation, the data given in the above table confront us with another significant difficulty, namely, how to account for the greater effect of acetic and formic acids on the electrical charge of the particles. It is not infrequently that mention is made of the independent adsorption of ions meaning thereby that the adsorbability of an ion of one kind is independent of the nature of other ions present in the liquid. It is not possible to account for the peculiarities just mentioned from this point of view, unless we assume that the order of adsorbability of anions is as follows :—

Chloride > Oxalate > Formate > Acetate.

This order is the reverse of what one finds in coagulation

experiments (Mukherjee and Chaudhuri, *loc. cit.*). For those who believe in the independent adsorption of ions irrespective of the role of electrostatic forces, the only possible way out of this difficulty would lie in the assumption that electrical charge of colloidal particles has nothing to do with the adsorption of ions. Otherwise, as we have just seen, we arrive at conclusions which contradict each other. It might be suggested that neutral molecules of these acids are adsorbable to a greater extent than the anions which are present on the surface and have imparted a charge to it with the result that these *neutral* molecules displace them from the surface and lower the charge. *Against this point of view* lies the fact that such an assumption should lead us to expect a lowering of the stability of the colloid ; alternatively, the facts can be explained by assuming that such an adsorption increases the stability of the sol, though it decreases the charge.

The lower rate of migration observed with these acids cannot be accounted for on the ground of the change of viscosity as the colloid-acetic acid and the colloid-hydrochloric acid mixtures show only slight difference in this respect (about 3 per cent.).

Oxalic acid shows a more complicated behaviour. Below a certain hydrogen ion concentration, the negative charge is greater in the case of oxalic than in the case of hydrochloric acid. Above it the reverse takes place. Here also a lower charge corresponds to a greater stability as the coagulating power of oxalic acid is lower than that of hydrochloric acid. The sols with which Mukherjee and Chaudhuri worked contained free arsenious acid and for reasons given in an earlier part of this work, the absence of polythionic acids is to be assumed. So the peculiarities cannot be referred to the interaction between polythionic acids and hydrogen ions.

A simple explanation, however, suggests to ourselves from the point of view that the adsorption of ions is not independent, but that a surface, which owes its charge to the adsorption of anions, can as a result of electrostatic forces take up oppositely charged ions by 'electrical adsorption' as defined by one of us. If the surface exerts no chemical affinity on the oppositely charged ion, then the electrical forces determine its adsorbability. In a previous paper (*Trans. Far. Soc., loc. cit.*) the electrical adsorbability of an oppositely charged ion was stated to be determined by w , the electrical work necessary to separate it from the surface.

$$w = \frac{n_1 n_2 E^2}{x D}$$

where n_1 is the valency of the primarily adsorbed ion and n_2 that of the oppositely charged ion; E is the electronic charge, x , the distance separating the centres of the two ions and D , the dielectric constant.

We have reasons to believe that in a large number of cases, oppositely charged ions are adsorbed on the surface in a solvated condition as opposed to what might be called adsorption of *anhydrous* ions. If, therefore, n_1 , n_2 and x remain constant, the adsorbability of the ion will increase, as the dielectric constant decreases. The cataphoretic velocities according to Helmholtz and Lamb are given by the following equations:

$$V = \frac{k(\phi_i - \phi_a)}{4\pi\eta} \quad \dots, \text{Helmholtz}$$

$$V = \frac{k(\phi_i - \phi_a)}{4\pi\eta} \times \frac{l}{d} \quad \dots, \text{Lamb}$$

The potential of the double layer $(\phi_i - \phi_a)$ is directly proportional to the density of electrical charge and

inversely proportional to the dielectric constant. According to both equations the cataphoretic velocity per unit potential gradient is proportional to the density of the electrical charge on the surface and is independent of the dielectric constant of the medium (assuming l/d to be constant in the Lamb equation).

Our conception regarding electrical adsorption leads us to expect that, other factors remaining constant, the velocity of the migration for the same hydrogen ion concentration (activity) will be smaller, the lower the dielectric constant.

Now acetic and formic acids in the pure state have dielectric constants 9.7 and 58.5 at 18° and 16° respectively (Landolt-Börnstein, *Physikalisch Chemische Tabellen*, p. 1218). It is quite reasonable to assume that solutions of acetic acid or formic acid containing a fair proportion of undissociated acetic or formic acid molecules will have a dielectric constant lower than water. Unfortunately there are no data on this point. Moreover a diminution in the dielectric constant can account for the increased stability of the sol against precipitation by electrolytes. In the foregoing pages we have said that the percentage of successful collisions depend on the work against electrical forces associated with coalescence. Other things remaining constant if the dielectric constant diminishes, the electrical work involved in the displacement of electrical charges will also increase. The percentage of successful collisions will diminish rapidly in view of the exponential relations between the electrical work and the rate of coalescence (Mukherjee and Mazumdar, *loc. cit.*).

The diminution of the dielectric constant in the medium would therefore produce two effects—one tending to diminish and the other to increase the stability against precipitation by electrolytes. It is possible to conceive

that the net result in some cases will be an increase and in other cases a diminution in stability. We have made some observations in support of this statement.

The influence of the dielectric constant which we have just discussed does not preclude an actual increase in the negative charge at low concentrations of an acid owing to the adsorption of its anions (as has been suggested by Freundlich) if the dielectric constant of the medium^{*} is not much different from that of pure water. Probably some such thing happens in the case of oxalic acid; at low concentrations the number of undissociated molecules is less and the dielectric constant is not probably much different from that of water and so we observe an increase in the migration velocity from the adsorption of anions.

In conclusion we would state that the explanation we have advanced is the only one that suggests to us and can account for all of our observations. At the same time we recognise that to substantiate it, further experiments are necessary. Such experiments are in progress.

Summary.

(1) The variation of the charge of colloidal arsenious sulphide with different concentrations of various acids depends on the nature and the method of the preparation of the sols.

(2) A simple behaviour is exhibited only by those sols which contain arsenious acid in excess. The irregularities observed are probably to be attributed to an interaction between polythionic acids and hydrogen ions present in the sols.

(3) For the same hydrogen ion concentration (activity) acetic and formic acids lower the charge to a

greater extent than oxalic and hydrochloric acids. The explanation is advanced that due to the lower dielectric constants of acetic and formic acids, electrical adsorbability as defined by one of the authors increases and the charge correspondingly decreases.

(4) It has been observed that though acetic and formic acids lower the charge to a greater extent than hydrochloric acid, the coagulating power of the latter is greater and the order of coagulating power is the reverse of the order of the capacity to diminish the charge. This fact is also explained as the result of the diminution of the dielectric constant.

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The Relation between the Surface Tension and Viscosity of Liquids.

Part I.

BY

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Porter (*Phil. Mag.*, 23, 458) finds that if the viscosities of two liquids be determined over a very large range of temperature, certain temperatures can be found at which their viscosities are the same and if a curve be plotted with T and T/T_0 , where T and T_0 are the absolute temperatures at which their viscosities are the same, a straight line is obtained.

Similarly, if we determine the surface tension of two liquids over a very large range of temperature, certain temperatures can be found at which their surface tensions are the same and if a curve be plotted with T and T/T_0 , a straight line is obtained. As an example we take chlorobenzene and diethyl ether :—

No.	Temperature of chlorobenzene	Temperature of ether	Surface tension.	T/T_0
1.	150°	66°	17.67	1.2471
2.	200°	101°	12.72	1.2641
3.	250°	143°	8.04	1.266
4.	300°	180°	3.79	1.264

An attempt has been made to find a relationship between surface tension and viscosity. Water, methyl alcohol, ethyl alcohol, benzene and acetic acid have been considered. The values for surface tension and viscosity have been taken from the tables of Landolt and Börnstein.

It is found that if the logarithm of viscosity be plotted against the logarithm of surface tension, a straight line is

obtained, and the following general equation is applicable to ethyl and methyl alcohols, benzene and acetic acid.

$$\log \lambda = M \log \mu + C$$

where λ represents surface tension; M is the slope which the straight line makes with the positive direction of the x axis; μ represents viscosity; C is the intercept which the straight line makes with the y axis.

The equation fairly holds good for water also.

Ethyl Alcohol.

No.	Temperature	Viscosity	Surface tension	
			Observed	Calculated
1.	10°	0.01450	23.35	23.35
2.	20°	0.01190	22.03	22.11
3.	30°	0.00989	21.13	21.52
4.	40°	0.00827	20.20	20.03
5.	50°	0.00697	19.25	19.13
6.	60°	0.00591	18.43	18.29
7.	70°	0.00501	17.53	17.53

Calculated from $\log \lambda = 0.2713 \log \mu + 0.5102$.

Summary.

1. If the surface tensions of two liquids be determined over a large range of temperature, certain temperatures can be found at which their surface tensions are the same, and if a curve be plotted representing the ratios of their absolute temperature against the absolute temperatures of the others, a straight line is obtained.

2. When the logarithm of surface tension is plotted against the logarithm of viscosity a straight line is obtained.

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Studies in Heterocyclic Compounds.

Part I.

BY

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The number of known compounds containing two dissimilar heterocyclic rings in their molecules is not great and it was thought interesting to study how in such compounds the properties of the different heterocyclic nuclei were affected by one another.

Aromatic *ortho*-diamines like *o*-phenylenediamine being well adapted for the formation of heterocyclic compounds, 2:3-diamino-phenazine (Ullmann and Mauthner, *Ber.*, 1902, 35, 4302), which already contains one heterocyclic ring, was chosen as the starting material. The idea was to introduce various types of new heterocyclic rings through the two *ortho*-amino groups and find out how the properties of the already existing azine ring were influenced by the newly entering hetero-ring and *vice versa*.

It has now been found that 2:3-diamino-phenazine is not so well adapted as *ortho*-phenylenediamine for the formation of heterocyclic compounds. Evidently the existing azine ring in the molecule influences the otherwise easily reactive *ortho*-amino groups.

2:3-Diamino-phenazine has now been condensed with phthalic, camphoric, 1:8-naphthalic and diphenic anhydrides (*cf.* Rupe and Thiess, *Ber.*, 1909, 42, 4287; Sachs, *Annalen*, 1909, 365, 117). On an examination of the properties of the acidoylene-phenazino-iminazoles so obtained it is found that in their molecules the properties of the heterocyclic azine ring are to some extent modified by the introduction of the acidoylene-iminazole ring and

vice versa. They are all yellow, *i.e.*, possess almost the same colour as diamino-phenazine.

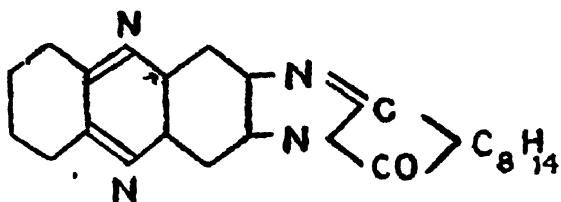
2:3-Diamino-phenazine has also been condensed with benzaldehyde, anisaldehyde, *m*-nitrobenzaldehyde and *p*-dimethyl aminobenzaldehyde and the properties of the resulting iminazoles studied.

An attempt was next made to prepare $\alpha\beta$ -diketo-2:3-phenazino-dihydroquinoxaline by the condensation of 2:3-diamino-phenazine with oxalyl chloride and introduce further heterocyclic rings through the *o*-diketonic group of that body; but the condensation product probably tautomerises readily to the dihydroxy-quinoxoline form and therefore does not show any of the reactions characteristic of the *ortho*-diketones. Attempts to condense *o*-phenylenediamine with the dihydroxy-azino-azine were also unsuccessful.

2:3-Diaminophenazine and nitrous acid form an azoimide derivative fairly easily. But it does not form cyclic guanidine derivative with mustard oils. With *o*-tolyl mustard oil it yields a thiourea derivative. Iminazole derivatives were not obtained by the action of either acetic anhydride (*cf.* Fischer and Hepp, *Ber.*, 1889, 22, 357) or benzoylchloride on 2:3-diaminophenazine. Chlorocarbonic ester or sulphur dioxide has no action on the diaminophenazine.

EXPERIMENTAL.

o-Camphoroylene-2:3-phenazino-iminazole.



An intimate mixture of 2:3-diaminophenazine (1 gm.) and camphoric anhydride (1.5 gms.) was heated

under reflux in an oil-bath to 240°, when it melted. The temperature was then quickly lowered and kept at 210° for half an hour. After cooling, the melt was repeatedly extracted with ether. The solid obtained on evaporating the ethereal solution was boiled several times with water and filtered hot. The residue separated from dilute alcohol in beautiful yellow needles, melting at 215-219° with previous shrinking at 202°.

It is insoluble in water, but soluble in ether or alcohol. It gives a greenish-black colouration with strong sulphuric acid (Found : N=15·75. C₂₂H₂₀ON₄ requires N=15·73 per cent.).

o-Benzoylene-2:3-phenazino-iminazole.

The light-green mass, produced by heating 1 gm. of 2:3-diaminophenazine and 1 gm. of phthalic anhydride for two hours at 210-230° after having been repeatedly boiled with water and then thoroughly washed with warm glacial acetic acid, crystallised from nitrobenzene in bright-yellow needles, not melting below 300°.

It is insoluble in water or ether, very slightly soluble in alcohol, benzene or acetic acid, and readily soluble in pyridine or nitrobenzene. With concentrated sulphuric acid it gives an intense red colouration (Found : N=17·92. C₂₀H₁₆ON₄ requires N=17·39 per cent.).

o-Naphthoylene-2:3-phenazino-iminazole.

The mass produced by heating 2:3-diaminophenazine (1 gm.) and naphthalic anhydride (1·5 gms.) under reflux at 270°-280° for one hour and a half was successively boiled with alcohol and glacial acetic acid and filtered hot. The residue crystallised from nitrobenzene as bright-yellow needles, not melting below 300°.

It is insoluble in water, ether, alcohol or acetic acid, slightly soluble in pyridine. It dissolves in concentrated

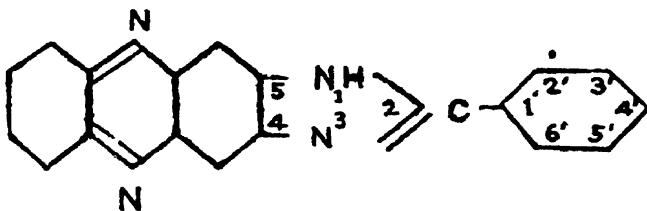
sulphuric acid with a deep-violet colour (Found : N = 15.09. C₂₄H₁₂ON₄ requires N = 15.05 per cent.).

o-Diphenoylene-2:3-phenazino-iminazole.

The greenish mass produced by heating a mixture of 2:3-diaminophenazine (1 gm.) and diphenic anhydride (1.5 gms.) for one hour at 220°-240°, after having been boiled several times with alcohol and then thoroughly washed with hot pyridine, crystallised from nitrobenzene as greenish-yellow needles, not melting below 290°.

It is insoluble in ether, alcohol or pyridine but readily soluble in nitrobenzene. With concentrated sulphuric acid it gives a blood-red colouration (Found : N = 13.94. C₂₆H₁₄ON₄ requires N = 14.07 per cent.).

4:5-Phenazino-2-phenyliminazole.



2:3-Diaminophenazine (0.5 gm.) and 30 c.c. of benzaldehyde were heated until the solid completely dissolved, when on cooling brown crystals separated. These were filtered, washed with ether and finally recrystallised from alcohol in beautiful, brown, shining needles, not melting below 290°.

It dissolves in alcohol with green fluorescence. It is insoluble in water and soluble in benzene. With strong sulphuric acid it gives a blood-red colouration (Found : N = 18.61. C₁₉H₁₂N₄ requires N = 18.92 per cent.).

4'-Methoxy-4:5-phenazino-2-phenyliminazole.

A mixture of 2:3-diaminophenazine (1 gm.) and anisaldehyde (5 c.c.) was gently heated until the solid

dissolved and then boiled for one minute. The brown precipitate, obtained by adding ether to the cooled solution, separated from nitrobenzene in orange-yellow rectangular plates, not melting below 270°.

It is insoluble in water or ether but soluble in alcohol, acetic acid, nitrobenzene or pyridine. It dissolves in warm dilute caustic soda solution with a red colour and in strong sulphuric acid with a deep-blue colour. (Found : N=17·03. C₂₀H₁₄ON₄ requires N=17·17 per cent.)

3'-Nitro-4 : 5-phenazino-2-phenyliminazole.

The black precipitate, produced by heating for four minutes a mixture of separate solutions of 0·5 gm. of 2:3-diaminophenazine in 40 c.c. of hot water containing 2 c.c. of concentrated hydrochloric acid and 0·8 gm. of *m*-nitrobenzaldehyde in 30 c.c. of hot water containing 1 c.c. of alcohol, was first boiled with dilute ammonia for half an hour and finally crystallised from nitrobenzene in clusters of orange-yellow needles not melting below 300°.

It is insoluble in water or dilute hydrochloric acid, moderately soluble in alcohol and soluble in nitrobenzene or acetic acid. Warm caustic soda solution dissolves it with a red colour. (Found : N=20·00. C₁₉H₁₁O₂N₅ requires N=20·52 per cent.).

4'-Dimethylamino-4:5-phenazino-2-phenyliminazole.

The precipitate, produced by heating 0·5 gm. of the phenazine and 0·8 gm. of *p*-dimethylaminobenzaldehyde in 64 c.c. of water containing 4 c.c. of concentrated hydrochloric acid for 15 minutes, after having been freed from hydrochloric acid by boiling with ammonia, separated from nitrobenzene in chocolate-red shining needles, not melting below 290°.

It is insoluble in water, ether or dilute hydrochloric acid, difficultly soluble in alcohol, and readily soluble in

acetic acid, pyridine or nitrobenzene. With concentrated sulphuric acid it gives a blood-red colouration. (Found : N = 20·42. C₂₁H₁₇N₅ requires N = 20·64 per cent.).

Dihydroxy-phenazino-quinoxoline. :

The dark solution produced by heating 0·5 gm. of 2 : 3-diaminophenazine and 2 c.c. of oxalyl chloride in 80 c.c. of boiling nitrobenzene for 15 minutes was filtered hot and it deposited, on dilution with ether, a brown precipitate which could not be crystallised. It was purified by repeatedly dissolving in dilute ammonia and precipitating by dilute hydrochloric acid; m. p. above 280°. It is insoluble in the common organic solvents. It dissolves in dilute ammonia or caustic soda solution. With concentrated sulphuric acid it gives a blood-red colouration. (Found : N = 21·52. C₁₄H₈O₂N₄. requires N = 21·21 per cent.).

2 : 3-Phenazino-azoimide.

2 : 3-Diaminophenazine (1 gm.) dissolved in 100 c.c. of water containing 5 c.c. of strong hydrochloric acid was diazotised in the usual way with 3 gms. of potassium nitrite. The reaction mixture was then allowed to stand at the ordinary temperature (33°) until the evolution of nitrogen oxide ceased. The precipitate obtained was washed first with water, then with a solution of sodium acetate and again with water, and finally crystallised from nitrobenzene in golden-yellow shining needles, melting at 280°.

It is practically insoluble in water, ether, alcohol, acetic acid or dilute hydrochloric acid but soluble in pyridine or nitrobenzene. It dissolves in dilute caustic soda solution with a deep-red colour and in strong sulphuric acid with a blood-red colour. (Found : N = 31·01. C₁₂H₇N₅ requires N = 31·67 per cent.).

2-o-Tolylureide of 3-Aminophenazine.

The precipitate, which separated on adding water containing a little common salt to the solution obtained by boiling 1 gm. of 2 : 3-diaminophenazine and 1.5 gms. of *o*-tolyl mustard oil in 50 c.c. of glacial acetic acid for half an hour, crystallised from alcohol in violet needles, not melting below 300°.

It is soluble in alcohol, hot water or dilute hydrochloric acid. It gives a green colouration with concentrated sulphuric acid. (Found : N = 19.91. C₂₀H₁₇N₅S requires N = 19.47 per cent.).

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Dithiocatechol.

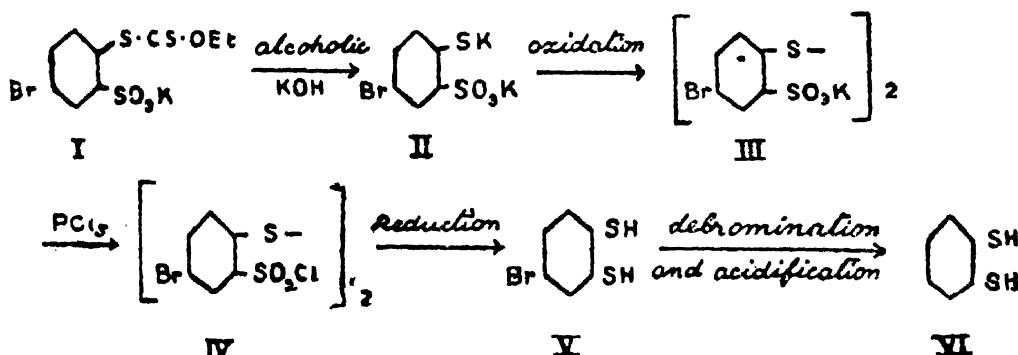
BY

PRAPHULLA CHANDRA GUHA AND MANINDRA NATH
CHAKLADAR.

Although dithiocatechol has been described (Pollak, *Monatsh.*, 1913, 34, 1673), its activity towards ring-closing agents has not been recorded. The present work was undertaken with a view to synthesise various ring compounds of sulphur derived from dithiocatechol. Dithiocatechol was originally obtained by Pollak (*loc. cit.*) by the reduction of benzene *o*-disulphonic acid. We

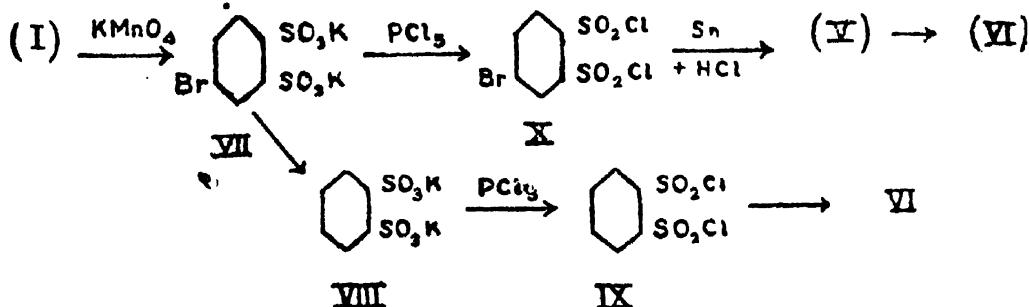
have, however, prepared the mercaptan by three different methods outlined below.

(i) 2-Xantho-5-bromo-potassium benzene sulphonate (I) is prepared from acetanilide according to the method of Armstrong and Napper (*Proc. Chem. Soc.*, 1900, 16, 160), hydrolysed to the dipotassium salt of 5-bromo-2-thiol-benzene sulphonic acid (II), oxidised to 5:5'-dibromo 1:1'-disulpho-diphenyl-2:2'-disulphide (III)—this step is necessary as otherwise the free mercaptanic group would interfere with the formation of the sulphochloride in the next step—which yields the corresponding disulphochloride of dibromodiphenyl disulphide (IV), which, subjected to the reducing action of tin and hydrochloric acid, yields two molecules of 1-bromo-3:4-dithiocatechol (V), and this bromo-mercaptan is finally debrominated by the action of zinc dust and alkali to the alkali salt of dithiocatechol, from which acid liberates the free dimercaptan (VI).



(ii) The second method consists in treating the xanthate compound (I) with potassium permanganate when the xanthate portion is oxidised to a sulphonic acid group giving rise to bromobenzene-*o*-disulphonic acid (VII), which is debrominated to yield the potassium salt of benzene-*o*-disulphonic acid (VIII), the chloride (IX) of which is finally reduced to dithiocatechol. A red solid is formed as an intermediate product which is further

reduced with difficulty and is supposed from its properties to be the lactone * of 1-thiol-2-sulphonic acid of benzene, the formation of which proves that the reduction proceeds step by step.



The production of this stable substance was really puzzling and more than once led the present authors to believe that dithiocatechol could not be prepared by this method.

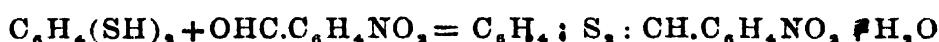
(iii) Sulphur has long been employed for the preparation of the aromatic mercaptans (Friedel and Crafts, *Compt. rend.*, 86, 884; Hofmann, *Ber.*, 1894, 27, 2807; Hinsberg, *Ber.*, 1905, 38, 1337; Hatinger, *Monat.*, 1883, 4, 165). In the present instance, it has been found that by heating together sodium-thiophenate and sulphur at high temperatures, a mixture of several compounds (sulphides, disulphides, etc.) is formed from which dithiocatechol can be obtained by reduction and fractional distillation.

Of the above three methods, the first and the second are decidedly superior to the third one. The success of the first method mainly depends upon the step by which the compound (I) is hydrolysed to the compound (II). It should also be mentioned here that the isolation of dithiocatechol from the mixture obtained in method (iii) would not have been possible but for the knowledge about its nature and physical properties previously

* The supposed thiolactone is under investigation.

gathered from a pure sample prepared by other methods.

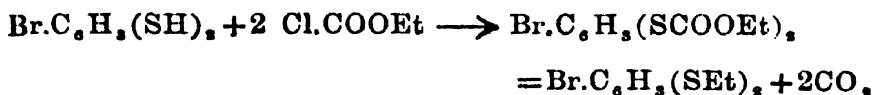
Besides preparing a dibenzoyl derivative and a disulphide of dithiocatechol, it has been condensed with *o*-nitrobenzaldehyde and acenaphthaquinone. One molecule of the nitrobenzaldehyde reacts with one molecule of the dimercaptan, thus,



In the case of acenaphthaquinone, only one ketonic group reacts with one molecule of the dimercaptan to give a mono-mercaptopol:

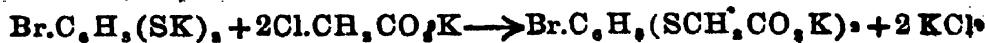


It was anticipated that chlorocarbonic ester would react with the dimercaptan to give either a dicarbethoxy compound $\text{Br.C}_6\text{H}_5(\text{SCOOEt})_2$ or a thiocarbonate $\text{Br.C}_6\text{H}_5:\text{S}_2:\text{CO}$ as has been observed in the case of catechol, but it has been found in actual practice that the expected dicarbethoxy compound first formed loses two molecules of carbon dioxide to give rise to a diethyl thioether, thus :

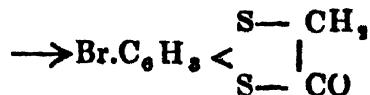
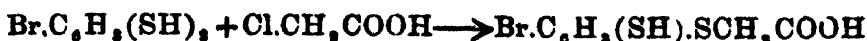


A similar phenomenon was observed by Dixon (*J. Chem. Soc.*, 1903, 83, 550) and by Wilson and Burns (*J. Chem. Soc.*, 1922, 122, 872). That the compound so formed in this reaction is really a diethyl-thiol derivative has been easily proved by preparing the same compound by the action of ethyl bromide on the dimercaptan.

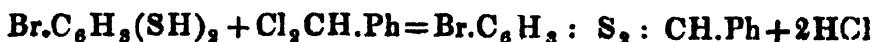
The potassium salt of bromo-dithiocatechol reacts very readily with potassium monochloracetate to give the potassium salt of bromophenylene-dithiodiglycollic acid,



from which the free acid is liberated by hydrochloric acid. If, however, the free acid is taken instead of the potassium salt and the mixture heated, the reaction proceeds in an entirely different way and a thio-lactone* is formed thus :

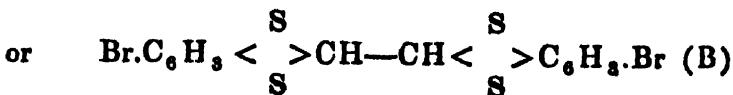
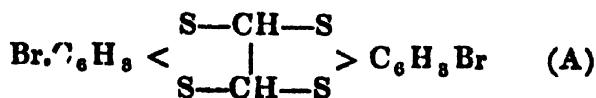


Benzal chloride reacts with the dimercaptan in the ordinary way to give benzylidene-bromodithiocatechol, thus :



The same compound has also been obtained from benzaldehyde and the dimercaptan.

The action of acetylene tetrabromide is interesting as it reacts with two molecules of the mercaptan. The product may be represented by one of the following formulæ :

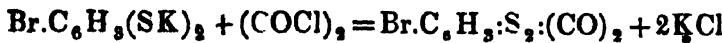
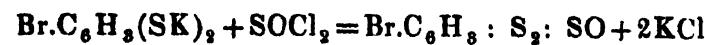


By analogy with the formula ascribed to the corresponding compound of catechol (*Bull. Soc. Chim.*, 3, 21, 101, 106), the authors are inclined to give preference to formula (A).

The action of acid chlorides, *viz.*, thionyl chloride and oxalyl chloride has also been studied and compounds quite

* For the analogous compound of catechol, *vide* Ludewig (*J. pr. Chem.*, 1900, 61, 345).

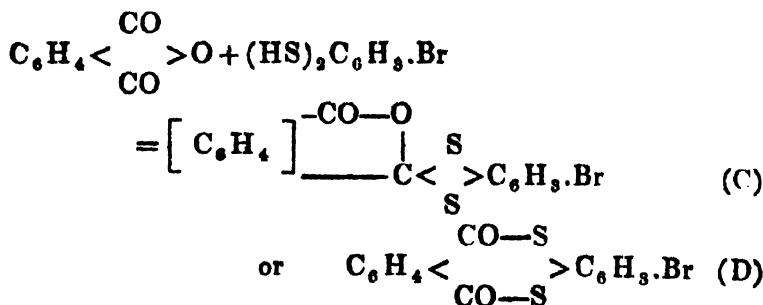
similar to those of catechol (*Ber.*, 1894, 27, 2752; 1890, 23, 1223) have been obtained :



No compound of catechol with thiophosgene is known, but the expected compound of brom-dithiocatechol is formed thus :

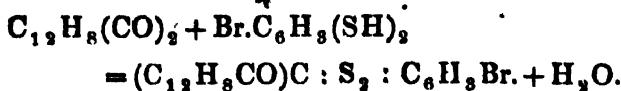


Though catechol gives two anthraquinone dyes, *viz.*, alizarine and hystizarine with phthalic anhydride (Bayer and Caro, *Ber.*, 1874, 7, 968), bromo-dithiocatechol reacts with the anhydride in an entirely different fashion due to the high reactivity of the thiol groups, and an alkali-insoluble compound is formed which may be represented by one of the following two formulæ (C) and (D).



As the compound is hydrolysed even on boiling with acetic acid, the authors are inclined to give preference to (D).

One molecule of phenanthraquinone reacts with one molecule of the dimercaptan, when boiled under reflux in alcoholic solution, yielding a monomercaptol :



If, however, the reaction is brought about in a sealed tube in presence of alcoholic hydrochloric acid, the dimercaptol $\text{C}_{12}\text{H}_8(\text{C} : \text{S}_2 : \text{C}_6\text{H}_3\text{Br})_2$ is formed.

EXPERIMENTAL.

1-Bromo-4-xantho-benzene-5-potassium sulphonate (I).

Twenty-five grams of the potassium salt of *p*-bromaniline-*o*-sulphonic acid * prepared according to the method of Caries (*Annales*, 286, 381) and 5 gms. of potassium nitrite were dissolved in water, cooled to 0° and 7 c. c. of sulphuric acid (1.84) diluted to 150 c.c. very slowly added with constant stirring. Gradually the diazo-anhydride separated out; it was rapidly filtered from the solution and washed with water containing ice until free from acid. It was then intimately mixed with a saturated solution of 15 gms. of potassium ethyl xanthate when there was a spontaneous evolution of nitrogen. In order to complete the reaction, the product was warmed up to 70° for about half an hour, a slightly yellow crystalline precipitate was obtained on cooling. It was crystallised from hot water; yield about 80%.

1-Bromo-4-thiolbenzene-5-potassium sulphonate and its Oxidation to the Disulphide.

Twenty grams of 1-bromo-4-xantho-benzene-5 the potassium sulphonate (I) were gently warmed with potassium hydroxide solution (5 gms. in 200 c.c.) for about an hour when it was hydrolysed to the thiol compound, which was partially transformed by aerial oxidation to the disulphide. Air was passed through the solution for a long time to convert the whole of the thiol compound into the disulphide. The solution was then concentrated and the crystalline mass, which separated out, was filtered off and dried. The free acid and its potassium salt are both very soluble in water.

* No description whatsoever is given in the original paper about the preparation of benzene-*o*-disulphonic acid from *p*-bromacetanilide. The present authors had to overcome all the experimental difficulties and to find out the actual methods and that is why the details of preparation are described in this paper.

4:4'-Dibromo-2:2'-disulphochloride of Diphenyl Disulphide.

Ten grams of the potassium salt of dibromo-diphenyl-disulphide-disulphonic acid were thoroughly dried and intimately mixed with 20 gms. of phosphorus pentachloride and heated on the water-bath for 4 to 5 hours with occasional shaking. The semi-solid mass was then poured on to ice. The separated chloride was filtered off, washed with cold water and crystallised from benzene. The yield was 9 gms.

*Reduction of the above Sulphochloride : Formation of
1-Bromo-3:4-dithiocatechol.*

Ten grams of the above chloride were finely powdered and heated with 40 gms. of tin and an excess of conc. hydrochloric acid. After 5 to 6 hours the whole was converted into an oil which was separated by steam distillation. The oil solidified to a crystalline mass as it dropped into the receiver and was purified by precipitation from an ice-cold alcoholic solution by the addition of ice-cold water. It forms a bright yellow lead mercaptide and a pale yellow mercury mercaptide. Iodine throws down the disulphide as an amorphous precipitate from an alcoholic solution of the substance. It is very soluble in alcohol and ether, and melts at 43-44°. (Found : C=32.49 ; H=2.37 ; Br=35.98 ; S=29.13. $C_6H_5S_2Br$ requires C=32.5S ; H=2.62 ; Br=36.24 and S=28.95 per cent.).

*Debromination of the Dimercaptan by Zinc Dust and
Caustic Potash : Formation of free Dithiocatechol.*

Twenty grams of 1-bromo-3 : 4-dithiocatechol were dissolved in a solution of 5 gms. of caustic potash, and the solution was heated with 4 gms. of zinc dust for 9-10 hours over a free flame. After removing the zinc

by filtration, the solution was acidified with hydrochloric acid, when an oil separated out which was extracted with ether, dried over anhydrous potassium sulphate, the ether driven off, and finally the oil was distilled. The distillate, coming over between 235° and 238° , was collected. It was redistilled and the fraction between 238° and 239° was retained. It is a colourless transparent oil possessing a mild smell resembling that of thiophenol. It is very soluble in alcohol and ether. It solidifies at $28\text{--}29^{\circ}$. (Found: C=50·29; H=4·63; S=46·10. $C_6H_6S_2$ requires C=50·70; H=4·22; S=45·77 per cent.).

1-Bromobenzene-3 : 4-potassium disulphonate.

Bromo-xantho-benzene potassium sulphonate (I) was dissolved in boiling water and a concentrated solution of potassium permanganate was added to the solution until the colour of the permanganate persisted. The separated manganese dioxide was filtered off and the solution on concentration gave white crystals of the potassium salt which were filtered off and dried. The yield was quantitative.

1-Bromobenzene-3 : 4-disulphonyl chloride.

Twenty grams of the potassium salt of bromobenzene-*o*-disulphonic acid were thoroughly dried and intimately mixed with 36 gms. of phosphorus pentachloride and heated on a water-bath for 4 to 5 hours with frequent shaking. The semi-solid mass was then poured on to ice. An oil separated which solidified to a crystalline mass on standing. It was washed with cold water and crystallised from benzene. It melted at 100° and not at 104° or 85° as mentioned in *Annalen*, 198, 28 and *Proc. Chem. Soc.*, '16, 160 respectively.

Reduction of the above Compound : Formation of Bromo-dithiocatechol.

To a boiling mixture of 30 gms. of granulated tin and an excess of conc. hydrochloric acid, 10 gms. of the sulphochloride were gradually added. The sulphochloride melted and after three or four hours, the whole set to a solid lump which resisted further reduction even on prolonged heating with tin and hydrochloric acid. The red cake was well ground and again introduced into the reaction vessel. After the heating had continued for 5 to 6 hours more, the whole of the red powder disappeared and an oil separated which assumed a reddish tint on cooling, but on being heated again with tin and hydrochloric acid became colourless. The separated oil was distilled with steam and collected in an ice-cold flask where it solidified. The crystalline mass was rapidly filtered off, dissolved in ice-cold alcohol and precipitated with ice-cold water. Its properties are identical with those of bromo-dithiocatechol prepared by the previous method. The yield was 4 gms. (Found : C=32.27; H=2.51. $C_6H_5S_2Br$ requires C=32.58; H=2.26 per cent.).

Potassium benzene-o-disulphonate.

The preparation of benzene-o-disulphonic acid was first attempted from metanilic acid according to the method of Limprecht (*Ber.*, 1876, 9, 553). It was found that the separation of aniline-2 : 3-disulphonic acid from the 2 : 4-disulphonic acid is a very tedious process and the yield and purity of the substance obtained by this method was far from satisfactory. So, after working on this method for a considerable length of time, it had to be

* It was insoluble in all ordinary organic solvents, but soluble in caustic alkalis from which it was reprecipitated by acids as a red amorphous powder.

abandoned. The melting point of benzene-*o*-disulphochloride as obtained by Limpricht is given as 105°, but the disulphochloride described in the present paper and prepared according to the method of Armstrong and Napper melts at 143-144°. Evidently Limpricht's benzene-*o*-disulphochloride was impure and probably admixed with some *p*-disulphochloride due to imperfect separation of the parent disulphonic acids.

Twenty-five grams of 1-bromobenzene-3 : 4-potassium disulphonate were heated with 10 gms. of caustic potash, 8 gms. of zinc dust and 800 c.c. of water for 9 to 10 hours. The remaining zinc was filtered off, the solution was saturated with carbonic anhydride and the precipitated zinc carbonate filtered off. The solution on concentration gave crystals which were filtered off, dried and recrystallised from water. The yield was quantitative.

*Benzene-*o* disulphochloride.*

Thirteen grams of the sulphochloride were obtained from 20 gms. of potassium-benzene-*o*-disulphonate and 45 gms. of phosphorus pentachloride. It was crystallised from benzene. M. p. 143°.

Reduction of the above Sulphochloride : Formation of Dithiocatechol.

Ten gms. of the benzene-disulphonyl chloride were gradually added to a boiling mixture of 30 gms. of tin and excess of concentrated hydrochloric acid with constant shaking. Here also after 3 to 4 hours a red lump separated which after grinding and further boiling with the reducing agents disappeared, and an oil was formed, (which, on exposure to the air at ordinary temperature, was slowly transformed into a red powder).

The oil was distilled with steam and the distillate collected in a receiver cooled in ice where the oil solidified

and acquired a reddish tint. It was rapidly filtered off, dissolved in ice-cold alcohol and reprecipitated by the addition of ice-cold water. It was then kept in a vacuum desiccator where it melted to an oil again. The oil was finally purified by distillation. It boils at 238-239° and solidifies at 28-29°. (Found : S=45·63. C₆H₆S₂ requires S=45·77 per cent.)

Fusion of Sodium Thiophenate with Sulphur. Isolation of Dithiocatechol.

Twenty grams of perfectly dry sodium thiophenate were thoroughly mixed with 7 gms. of sulphur and the mixture was heated on an oil-bath at 170° to 180° for six hours. The fused mass was then treated with an excess of dilute sulphuric acid, when there was a profuse evolution of sulphuretted hydrogen and at the same time a dark brown oil of very unpleasant odour separated. The oil was subjected to steam distillation. A portion of the oil distilled over with steam while the greater part, being non-volatile, remained in the distilling vessel. The portion, that was volatile with steam, was found to be unconverted thiophenol.

The residual oil was extracted with ether. It was partly soluble in alkali but insoluble in acid. On allowing it to stand over-night in a vacuum desiccator it turned into a semi-solid mass, which was boiled under reflux with tin and hydrochloric acid for 10 hours and was then extracted with ether. The ether was evaporated off ; the residual oil in alcoholic solution gave a yellow lead mercaptide with lead acetate. This in alcoholic suspension was treated with sulphuretted hydrogen when it decomposed giving black lead sulphide, which was separated by filtration. The alcohol was distilled off and the residual oil distilled fractionally ; the portion boiling between 233° and 238° (about 5 gms.) was

redistilled, this time the fraction coming over between 238° and 239° was collected. The yield of the pure product was only 1.2 gms. The oil solidifies at $28-29^{\circ}$ and is identical with the sample of dithiocatechol prepared by other methods.

Oxidation of Dithiocatechol to its Disulphide.

To an alcoholic solution of the dithiocatechol alcoholic iodine was added in slight excess with shaking when a voluminous yellowish precipitate separated. The precipitate was filtered off and washed with alcohol, potassium iodide solution and finally water. It could not be further purified as it was insoluble in ordinary organic solvents. It melts at $185-190^{\circ}$. (Found : C=51.16 ; H=3.2. $C_6H_4S_2$ requires C=51.43 ; H=2.85 per cent.)

Dibenzoyldithiocatechol.

A caustic potash solution of 1 gm. of dithiocatechol was shaken with the calculated quantity of benzoyl chloride, when a solid substance separated out which was filtered off, washed with caustic potash solution and water, and crystallised from acetone. It melts at 77° . (Found : S=17.92. $C_{20}H_{14}O_2S_2$ requires S=18.28 per cent.)

o-Nitrobenzylidenedithiocatechol.

A mixture of 1 gm. of *o*-nitrobenzaldehyde, dithiocatechol and 25 c.c. of alcohol saturated with hydrogen chloride was heated in a sealed tube at 100° for 8 hours. After opening the tube the liquid was decanted from the pasty mass, which was then shaken with cold alcohol when shining crystals separated out. The crystalline product was filtered off, washed with cold alcohol and recrystallised from hot alcohol in shining yellow needles. It melts at 106° . (Found : N=5.2. $C_{18}H_9O_2NS_2$ requires N=5.09 per cent.)

Reaction with Acenaphthoquinone.

One gm. of dithiocatechol and 5 gms. of acenaphthoquinone were heated together in an alcoholic solution under reflux for 7-8 hours. The solution was filtered hot and yellow needles separated out from the solution on cooling. The product was recrystallised from alcohol. M. p. 190°. (Found : S=20·4. C₁₈H₁₆OS₂ requires S=20·9 per cent.)

Oxidation of Bromo-dithiocatechol : Formation of the Sulphide.

To an alcoholic solution of bromo-dithiocatechol alcoholic iodine solution was added in slight excess when a voluminous precipitate was formed. It was filtered off, washed with alcohol and potassium iodide solution and finally with water. It was insoluble in most organic solvents. It melts at 154°. (Found : C=32·58; H=2·1. C₆H₃S₂Br requires C=32·87; H=1·37 per cent.)

Dibenzoyl-bromodithiocatechol was prepared in the same way as the benzoyl derivative of dithiocatechol. It melts at 85°. (Found : S=14·4. C₂₀H₁₃O₂BrS₂ requires S=14·91 per cent.)

Bromodithiocatechol Diethyl Ether.

The potassium salt of 1-bromo-3 : 4-dithiocatechol (1·5 gms.) was dissolved in 50 per cent. spirit and ethyl bromide was gradually added to it with constant shaking, and the mixture warmed on the water-bath. A crystalline product was obtained from the solution on concentration and cooling which was recrystallised from weak spirit; m. p. 54°. (Found : C=42·99; H=5·1. C₁₀H₁₃S₂Br requires C=43·3; H=4·7 per cent.)

Reaction with Chlorocarbonic Ester : Formation of the Diethylether.

One molecular proportion of the potassium salt of 1-bromo-3 : 4-dithiocatechol was suspended in dry benzene, and two mols. of chlorocarbonic ester were added to it. The product was then heated for half an hour under reflux when CO_2 evolved. Potassium chloride was filtered off from the hot solution from which shining crystals were obtained on concentration and cooling. The compound was recrystallised from weak spirit. It melts at 54° . (Found : C=43·5; H=5·2. $\text{C}_{10}\text{H}_{13}\text{S}_2\text{Br}$ requires C=43·3; H=4·7 per cent.)

Reaction with Potassium Monochloracetate : Formation of 1-Bromobenzene-3 : 4-dithio-diglycollic Acid.

To an aqueous solution of 1·5 gms. of the potassium salt of bromodithiocatechol, 2 gms. of monochloracetic acid dissolved in potassium carbonate solution were added and slightly warmed. An amorphous precipitate was obtained from the solution on acidification. This was crystallised from water in shining white plates. The product dissolves in sodium carbonate liberating carbon dioxide. It melts at 170° . (Found : C=35·23; H=3·1. $\text{C}_{10}\text{H}_9\text{O}_4\text{S}_2\text{Br}$ requires C=35·6; H=2·6 per cent.)

Reaction with free Monochloracetic Acid : Formation of the Thiolactone (vide p. 322).

An aqueous solution of 1·5 gms. of the K-salt of bromo-dithiocatechol and 3 gms. of monochloracetic acid were boiled for about half an hour. The solution was then cooled and acidified with hydrochloric acid, when a white precipitate was obtained which crystallised from water with 2 molecules of water of crystallisation. It is soluble in caustic alkali, but does not liberate

carbon dioxide from sodium bicarbonate. It melts at 191°. (Found : C=32.5; H=3.81. $C_8H_5OS_2Br, 2H_2O$ requires C=32.32; H=3.0 per cent.)

Reaction with Benzalchloride : Formation of Benzylidene-bromodithiocatechol.

The method of preparation is exactly the same as for the following compound. It melts at 170°. (Found : C=50.1; H=3.51. $C_{13}H_{10}S_2Br$ requires C=50.32; H=2.91 per cent.)

Reaction with Acetylenetetrabromide : Formation of Glyoxal-dibromo-dithiocatechol.

The potassium salt of 1-bromo-dithiocatechol (1.5 gms.) and 2 gms. of acetylene tetrabromide were heated under reflux in toluene solution for 1 hour. The separated potassium chloride was filtered off. The solution gave an amorphous solid on dilution with petrol ether. It was crystallised from benzene in prisms. It is insoluble in alcohol and melts at 236-238°. (Found : S=26.89. $C_{14}H_8S_4Br_2$ requires S=27.59 per cent.)

Benzylidene bromo-dithiocatechol from Benzaldehyde and Bromodithiocatechol.

Molecular proportions of bromo-dithiocatechol and benzaldehyde dissolved in alcoholic HCl were heated in a sealed tube at 100° for 7-8 hours. The tube was then opened and the separated solid was filtered off, washed with alcohol and crystallised from benzene. M. p. 169-170°. Mixed m. p. with the product from benzal chloride 169-170°.

Reaction with Thionyl Chloride.

The potassium mercaptide (1.5 gms.) was gradually added to a toluene solution of 1.5 gms. of thionyl chloride, when a violent reaction ensued with the separation

of a yellowish white solid substance. The mixture was then heated under reflux for half an hour. The solid residue obtained on filtration was freed from KCl by washing with water and repeatedly washed with alcohol, and toluene. It was insoluble in all the common organic solvents, hence, it could not be crystallised. It melts with decomposition at 220° (Found : C = 27.3 ; H = 1.80. $C_6H_3OBrS_3$ requires C = 26.96 ; H = 1.12 per cent.)

Oxalo-bromodithiocatechol.

From 1.5 gms. of the potassium-dimercaptide and 0.5 gm. of oxalyl chloride 0.6 gm. of the oxalo compound was obtained. It was crystallised from a mixture of alcohol and benzene. The white crystalline product sublimes at 150° (Found : C = 34.61 ; H = 1.46. $C_8H_3O_2BrS_2$ requires C = 34.91 ; H = 1.08 per cent.).

Bromodithiocatechol Thiocarbonate.

The potassium mercaptide (1.5 gms.) and thiophosgene (1 gm.) were mixed together in toluene solution and heated under reflux for one hour and a half. The separated potassium chloride was removed by filtration. A reddish yellow precipitate was obtained from the filtrate when alcohol was added to it. It was boiled with bone-charcoal in acetone solution for about half an hour and filtered hot. The filtrate on concentration gave beautiful shining yellow needles, m. p. 140° . (Found : C = 31.51 ; H = 1.61. $C_7H_3BrS_3$ requires C = 31.51 ; H = 1.14 per cent.)

Reaction with Phthalic Anhydride.

A mixture of bromodithiocatechol and phthalic anhydride in molecular proportions was heated with fused zinc chloride at 125° to 136° for 3-4 hours. The product was then powdered and boiled with a large quantity of

water when a clear solution was obtained which was filtered hot. The filtrate gave shining needle-shaped crystals on cooling, which were recrystallised from water. The compound was insoluble in cold alkali and gave no precipitate with lead acetate. It is easily hydrolysed by acetic acid regenerating the mercaptan. (Found : S=17·9. $C_{14}H_7O_2S_2Br$ requires S=18·2 per cent.)

Phenanthraquinone Monomercaptol.

A mixture of 2 gms. of bromodithiocatechol and 1 gm. of phenanthraquinone was heated in alcoholic solution under reflux for 6 hours. The colour of the solution gradually disappeared and the whole set to a solid mass, which after filtration at the pump was crystallised from boiling acetic acid as a pale yellow crystalline powder. It melts at 195°. (Found : S=14·92. $C_{20}H_{11}OBrS_2$ requires S=15·57 per cent.)

Phenanthraquinone Dimercaptol.

One part of phenanthraquinone and two parts of bromodithiocatechol were heated in a sealed tube in presence of alcoholic HCl at 100° for 7-8 hours. The contents of the tube were filtered, concentrated and cooled, when a white crystalline product was obtained which was recrystallised from hot alcohol. It melts at 115°. (Found : S=20·1. $C_{26}H_{14}Br_2S_4$ requires S=20·8 per cent.)

This work is being continued.

Our thanks are due to Sir P. C. Rāy and Dr. J. C. Ghosh for the kind interest they have taken in this work.

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ERRATA.

Page 17, 18, 19 Tables VI to XII for "supernatent"
read "supernatant."

- 32 line 1* for "eamphene" read "camphene."
39 , 11* for "Point-o-lita" read "Point-o-lite."
63 , 10 for "Taluamidine" read "Toluamidine."
66 , 14* for "consideration" read "condensation."
73 , 11* omit "yellow."
73 , 10* insert "yellow" before "prismatic."

* from bottom.

